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VOL. 42 No. 391 JULY 1956

THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 14 March 1956, the Chair being taken by Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc., President of the Institute.

The General Secretary read the minutes of the meeting held on 8 February 1956, which were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting.

The Chairman introduced J. A. Shaw, who then presented the following paper in summary.

REFINERY UTILITY INSTALLATIONS *

By J. A. SHAW † (Associate Fellow)

SUMMARY

This paper sets out the principal considerations on which the design of the individual utility installations is based. A section of the paper is devoted to the pros and cons of power generation which so greatly affects the nature of the installation as a whole, and throughout an attempt is made to reveal the measures necessary to achieve that most essential quality, reliability.

INTRODUCTION

UTILITIES may be defined as accessory services required for the operation of all process units, and they comprise installations providing steam, electricity, water, fuel, and compressed air. The definition is sometimes extended to include fire fighting, effluent and waste disposal installations, chemicals, refrigeration, transportation, and communications, but for the purpose of this paper the first five items only are considered.

This is the simplest definition, but the utilities are also the life blood of a refinery, for not only can a defect in any one of them bring all processes to a standstill, but an upset arising from a process cause may also become a major disaster if the utility installations fail to meet the emergency demands. Reliability and flexibility are, therefore, the main criteria in the design of utility installations.

In discussing the individual utilities it is convenient to have as a basis for reference a hypothetical installation, which for the purpose of this study may be assumed to be a conventional 150,000-b.d. prime fuels refinery with crude distillation, catalytic cracking, reforming and polymerization units, and the associated finishing and offsite plant.

This hypothetical refinery will serve also as a framework on which to construct three alternative solutions to the power supply problem, so revealing some of the incentives and obstacles which confront the designer of utility installations.

THE COST AND SCOPE OF UTILITY INSTALLATIONS

In such a refinery, where all electric power is purchased, the capital cost of the utility installations might amount to some 15 per cent of the total investment.

If the whole of the power requirement were generated within the refinery this percentage would be considerably higher, as shown later in the paper.

In the case of a refinery where power is purchased the processing of each barrel of crude oil would entail the use of approximately:

100 lb of steam,
2 kW-hr of electricity,
600 gal of cooling water,
350,000 B.t.u. of fuel equivalent.

An attempt to split the consumption of individual utilities hypothetically among the various processes can be misleading, because both design and operational factors can have a considerable bearing upon the answer. Whereas, for example, a cat cracker might be a major steam consumer in one refinery, a basically similar unit could be a net steam producer in another, and the use of steam or electricity for pump and other drivers will depend to a large extent upon whether power is purchased or generated. In general, however, certain processes are potential steam consumers in that they have substantial heating requirements that can be most conveniently supplied by the use of steam, and among these may be numbered all processes dealing with light hydrocarbons and processes such as distillation in which steam is used for stripping. In cold climates a considerable steam consumption will also be attributable to tank, line, and space heating.

Large cooling water requirements are associated with power generation and such processes as catalytic cracking and catalytic reforming in which the large capacity compressors and blowers are often driven by condensing steam turbines.

* MS received 17 February 1956.

† Esso Petroleum Co. Ltd., Fawley Refinery.

INDIVIDUAL UTILITIES

Steam

Steam is the principal and most important utility in that it will be in greatest demand in the event of failure of one of the other utilities or during a fire or process upset, however caused.

The quantity and quality of steam required in any refinery depends to a large extent upon whether power is generated. Dry saturated steam at 120–200 p.s.i. will suffice for most process requirements. Whereas for power generation steam at 500–600 p.s.i. with 200° or more of superheat is customary.

The large turbines used for power generation call for a high degree of steam purity, and this factor coupled with the relatively high pressure of generation demands a boiler feed of prime quality and necessitates either a high proportion of condensate recovery or advanced water treating facilities.

On the score of steam purity, however, most process consumers are less exacting than power-generators, and the prime needs in process steam generation are for reliability and flexibility, the latter because of the very great steam loads that can result at short notice from plant upsets or from a fire.

Process consumers fall into two main categories, those from which condensate is recoverable and those from which it is not. The former category will include the larger drivers and those heating duties where the contamination of condensate by the product is impossible or unlikely and all tank heating and line tracing.

The condensing process drivers might produce condensate equivalent to about 30 per cent of the total process steam consumption, but most of this can be absorbed by process consumers, such as waste heat boilers.

Other sources of process condensate may produce a further 15–20 per cent which will be available for boiler feed, and there will also be a contribution from the steam used for feed heating, but a treated water make-up of some 70–80 per cent of the total feed will generally be required.

The exhaust steam from the smaller process drivers is usually discharged into a low-pressure system and used for various heating duties, the surplus being returned to the steam plant, where it is employed for feed water heating.

It is a feature of oil refineries that a surplus of not really marketable fuel exists on many occasions, and this factor coupled with the prime need for reliability, leads designers to the use of relatively simple water tube boilers without air heaters or economizers. This statement should not be interpreted as showing that fuel economy is a matter of no consequence in oil refineries, but rather that great economy is not usually sought at the expense of reliability which would probably be impaired by the use of air heaters or economizers having regard for the imperfect operating conditions. Superheaters are used to provide sufficient superheat only to ensure dryness at the extremities of the usually extensive distribution systems which may reach as much as one or more miles from the generating station. Superheaters of the drainable type are preferred because they will tolerate variations in steam purity arising from violent load changes and imperfect boiler feed. Feed deaeration and chemical conditioning are generally practised with a view to minimizing the corrosion of heat exchanger and condensate recovery equipment, and feed heating deaerators operating at suitable pressures can often be employed to utilize the heat in any surplus LP steam which would otherwise have to be condensed before inclusion in the boiler feed.

The high proportion of "make-up" required in the feed to the process steam generators necessitates relatively high blowdown rates, but the bulk of the heat so discarded can be recovered by the use of blow-down heat exchangers and flash steam collection.

The foregoing therefore, is a very general survey of the factors governing the design of process steam generating installations.

The unit size of refinery boilers varies between 100,000 and 300,000 lb/hr for process installations and up to as much as 500,000 lb/hr for power stations, the larger units being advantageous on a score of thermal efficiency and because they permit reduced operating and maintenance expenditure. The use of water walled furnaces, now almost universal in refineries, has greatly improved the flexibility of boiler installations, while permitting economies in the space occupied for a given capacity.

The specific heat release is kept low, to a maximum of about 200,000 B.t.u/cu. ft. furnace volume, so as to permit the burning of heavy residues, and both forced and induced draught fans are employed for the same reason.

Both separate and combination gas and oil burners are used, and steam atomization of the oil fuel is general.

A greater degree of instrumentation than is customary in other industries is desirable in an oil refinery because of the facility it affords for the handling of emergencies. The instrumentation frequently embraces the control of the dual firing system, but this feature will be described in greater detail at a later stage.

Figs 1 (*a*) and (*b*) illustrate alternative feed systems for a refinery process steam plant. Fig 1 (*a*) shows the vacuum deaerator system familiar in the U.K. and Fig 1 (*b*) the deaerating heater or pressure system which is characteristic of installations in the U.S.A. The principal advantage of the pressure system is that it permits the utilization of a greater quantity of surplus LP steam than is possible with the vacuum deaerator, and thus achieves a higher feed temperature. There is little to choose between the two systems on a capital investment basis, and it is to be hoped that the future will see increased use of the pressure deaerator, which is at present almost completely neglected by British manufacturers.

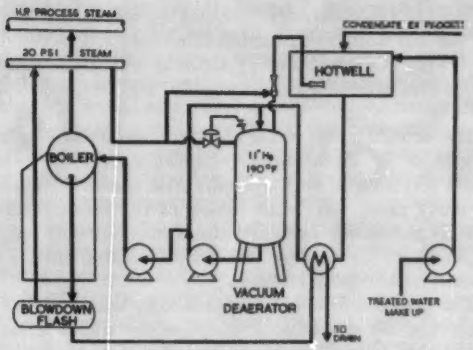

FIG 1 (*a*)

FEED SYSTEM WITH VACUUM DEAERATOR

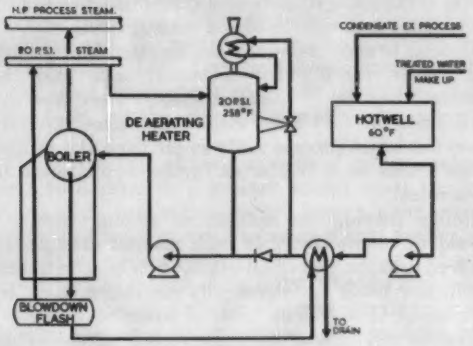

FIG 1 (*b*)

FEED SYSTEM WITH DEAERATING HEATER

Electricity

Electricity is employed primarily as motive power for process drivers and for lighting, and its application is therefore both vital and widespread. The reliability of the power supply system is of great importance, although an electrical failure of short duration need not be disastrous, provided the operation of the other utilities can be maintained throughout the emergency.

There are two basic solutions to the power distribution problem applicable to refineries where electric power is purchased.

They are the ring main system common in the U.K. and the radial secondary selective system more usual in the U.S.A.

Fig 2 illustrates a typical example of the latter system.

In essence this installation consists of an Electricity Authority substation supplied by two 132-kV feeders, in which the supply is transformed to 11 kV. From this point, the principle of duplication is preserved through the main 11/3·3-kV substations down to the unit substations in which the voltage is further transformed to 415 V, each of the duplicate transformers being large enough to carry the entire substation load in an emergency.

The consumers are shared approximately equally between the two transformers in each main and unit substation, and automatic bus-ties ensure that the effects of a fault occurring anywhere in the duplicated system are minimized in that motors which have been stopped by a fault on either side can be restarted a few seconds later.

All motors are fitted with over and under voltage trip delays, and it is usual for all but the largest motors to stay on the line during an automatic bus bar changeover.

Large motors operating at 3000 V are supplied directly from the 3·3-kV bus bars in the main substation, and most smaller drivers operating at 415 V are supplied from the unit or radial substations.

Single-phase supplies at 240 V for lighting are taken from the unit substations to suitable lighting panels, from which 100-V or 55-V supplies for hand tools can also be obtained by the use of local transformers.

Emergency lighting on the more important process units and utility installations is usually assured by the provision of small turbine- or diesel-driven generators fitted with automatic starting devices.

In refineries where power is generated internally, it is the modern tendency to transmit at 11 kV to the main substations, whereafter the system follows lines similar to those of the one already described.

Whether power is generated or purchased it is in the consumer's interest to operate at as high a power factor as possible, because by so doing he will make the best use of his electrical supply equipment. If power is purchased on a kVA basis as opposed to a kW basis an additional incentive for power factor improvement will exist. kW agreements, however, are rare, and most electricity boards in any case stipulate a minimum power factor at which the consumer must operate.

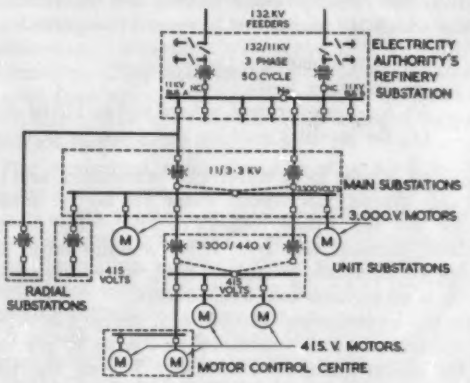

FIG 2

TYPICAL SYSTEM FOR DISTRIBUTION OF IMPORTED ELECTRIC POWER

In general, low power factors arise from a large proportion of the load being composed of small lightly loaded electric motors, welding loads, and fluorescent

lighting, so that a measure of control can be exercised at the design stage by care in sizing electric drivers. In refinery installations, however, considerations of reliability lead designers to load their electric motors fairly lightly so that other methods of power factor correction must be resorted to on occasion, and among these may be numbered:

(*a*) The use of suitably adjusted synchronous motors for the larger drivers.
(*b*) The use of static condensers.

Synchronous motors are objectionable on account of their bulk and because of their susceptibility to system disturbances, a feature which renders them unsuitable for duties where a brief interruption of the drive could have serious consequences.

The cost of synchronous motors is relatively high because of their associated exitation and starting equipment, and in most cases where an incentive for power factor improvement exists the installation of condensers will be justified.

Electric motors are still the cheapest and most convenient driver for all constant speed refinery equipment, and it is probable that their widespread use will continue for such applications where the power supply can be assured. Both domestic generation and purchased power installations can be made to have virtually 100 per cent reliability so that the choice of electric or other drivers becomes chiefly a question of convenience or the need to preserve a balance between HP and LP steam production. Some duplication of electric by steam drivers may, however, be considered justified for vital utility and process applications.

Water

In an oil refinery water is used for the following duties which are mentioned in order of magnitude:

(*a*) as a coolant;
(*b*) for boiler feed;
(*c*) for domestic uses, ashore and on board ship;
(*d*) for product washing and other process use.

For all but (*a*) fresh water will be required, and if a suitable source exists, fresh water will be the natural choice for the whole refinery supply. By far the greatest demand, however, is for cooling water, and where no adequate source of fresh water exists salt water is sometimes used as a coolant.

In the hypothetical 150,000-b.d. refinery in which all electric power is purchased and with 30 per cent of the steam going to condensing drivers, the total water demand might amount to as much as 100×10^6 g.p.d., and the process cooling water load would account for some 98 per cent of this total.

The next largest consumer, the boilers, would account for 90 per cent of the remainder, from which it is evident that these two fields offer the greatest scope for economy in design.

Cooling water systems can be sub-divided into two main categories:

(*a*) Once-through systems in which the whole of the water is discarded after use.
(*b*) Recirculatory systems in which the heated water is cooled evaporatively, and re-used.

The economies in water that can be effected by use of system (*b*) are obvious. Unfortunately, however, it is a requisite of such systems that the water should be fairly clean, and since much of the cooling water flow in a refinery becomes contaminated with oil, it is necessary to confine the use of cooling towers to certain clean water streams.

The position is altered appreciably where power is generated by condensing turbines or where a large number of these are used as drivers of process plant, for from 5 to 10 gal of water are required for the condensation of each 1 lb of steam, and the effluent from steam condensers is quite clean, and can therefore be recirculated indefinitely over a cooling tower.

Cooling towers, therefore, are an attractive proposition where there exists a considerable and concentrated source of clean effluent. They also find application in very large refineries, where expansion takes the latest process units so far from the primary water source as to render its further exploitation uneconomical.

Before leaving the subject of cooling towers, it should be mentioned that both natural draught and induced draught types find application in oil refineries, the former being more generally associated with large permanent installations, such as power stations.

The capital cost of the reinforced concrete natural draught tower is about 50 per cent higher than its induced draught counterpart on a basis of equal capacity, but the operating and maintenance costs of the latter are considerably higher, and on an amortisation basis there is little to choose between them.

Once-through systems are then the commonest solution for the refinery cooling water problem, the main difference between individual systems being in the nature of the pumping installation and the materials used for piping.

Where, because of an elevated or distant site, high pumping heads are involved, double pumping may be resorted to. Considerations affecting the choice of such a system are the cost of large diameter high pressure piping and the difficulty of combining high pump discharge heads with the very large capacities that will be required for refinery cooling duties. Where double pumping is employed, some form of storage capacity is frequently provided from which the secondary pumps take their suction. This arrangement has the advantage of providing at once a safeguard against temporary failure of the primary pumps and a conveniently situated reserve of water for fire fighting purposes.

Where possible simple horizontal, split casing, centrifugal pumps are favoured because of their inherent reliability and because of the ease with which they can be serviced, but where the need for high pumping heads is encountered multi-stage mixed flow or

centrifugal pumps are often used. Pumps of this kind are compact and flexible, and where they are designed for vertical installation a very neat and space-saving lay-out can be achieved. Their first cost, however, is relatively high, and their maintenance, costly and time consuming, particularly in the case of vertical installations. Vertically mounted multi-stage pumps are, however, attractive for jetty end installations, where space is at a premium and where foundation and construction costs are exceptionally high.

Wherever salt water is pumped, corrosion becomes a serious problem in both pumps and lines alike. The design of pumps, particularly as regards specific speed and head per stage, has great bearing upon their resistance to corrosion, for upon these factors depends the tendency toward cavitation under given suction conditions. Pumps of all types can, however, be made to give satisfactory service with salt water provided sufficient care is exercised in the choice of materials and, in particular, in the elimination of electrolytic couples. Certain stainless steels appear to be the most satisfactory materials for pumps in salt water duty, but the aluminium bronzes also give good service.

The suitability of cast iron as a pump material seems to depend to a greater extent upon the conditions of its use, and cases are known where single-stage volute type pumps having cast iron casings and aluminium bronze impellers have given long and satisfactory service in salt water duty, whereas high-speed mixed flow pumps of similar material specification and pumping the same water against a greater head have suffered severe electrolytic attack.

This experience suggests that while cast iron will give satisfactory service in salt water duty, so long as it is not subjected to the effects of high water velocity, its use is probably better avoided in high-head installations, although the severity of the duty in such cases might be reduced by increasing the number of stages.

The large diameter piping associated with refinery cooling water systems may account for as much as 30 per cent of the total cost of the installation, and it is therefore of interest to examine the respective merits of the alternative materials from which such piping can be constructed.

Cast iron piping, which is the most expensive of the alternatives, is widely used because of its inherent resistance to corrosion which renders it particularly suitable for buried service. Suitably jointed, it is suitable for any pressures likely to be encountered in refinery cooling water service, and it is relatively resistant to corrosion even without special treatment. The main disadvantages of cast iron piping are its high cost; the fact that it is not normally made in diameters exceeding 48 inches; and its relative mechanical weakness, necessitating very solid support to avoid damage by subsidence.

Steel piping, which is light, strong, and unrestricted as regards size or pressure rating, costs less than half as much as cast iron even when internally coated with bitumen. Where steel pipe is to be buried, however, the necessity for providing permanent protection against external corrosion will bring the total cost up to about the same level as that of cast iron piping. Proneness to corrosion is in fact the main disadvantage of steel piping and becomes a special problem in salt water service because the most economical of the protective coatings, bitumen, is itself vulnerable to attack by barnacles, which almost inevitably attach themselves to sections of line carrying clean salt water. Other protective linings suitable for steel piping are pressure applied cement and various synthetic rubbers.

Cement linings are unaffected by barnacles and are satisfactory provided a sufficient and uniform thickness can be obtained. It is extremely difficult to do this at joints and bends, where the special application machinery cannot be used, and failures of cement linings at such places do occur. Some but not all of the synthetic rubbers are resistant to barnacle attack, but their cost is at present so high as to raise the cost of internally protected steel piping above that of cast iron. The third alternative, pre-cast concrete piping, is suitable for very low pressure only, and shares with cast iron the disadvantage of comparative brittleness. It is, however, corrosion resistant, and since its cost is little more than one-quarter that of cast iron, it becomes an attractive proposition for the low pressure stages of multi-lift systems.

Figs 3 (*a*) and (*b*) show two alternative pumphouse arrangements for a tidal water source. A tidal variation of 15–20 ft would necessitate either of these pumphouses being located in fairly deep water if satisfactory suction conditions for the pumps are to be assured, and this factor will render their construction very costly.

The "dry" pumphouse which makes possible the use of horizontal split casing pumps, so desirable from a maintenance view-point, will be more costly than the alternative. This extra cost is in part due to the greater foundation area and in part to the need for providing a floor of sufficient beam strength to withstand the displacement upthrust.

The horizontal split casing pumps used in this scheme will, however, be less costly than the vertical pumps of the " wet " pumphouse, which if the delivery pressure is great may have to have two or more stages. Notwithstanding this fact, there will remain a substantial net cost differential in favour of the " wet " pumping installation.

It would be wrong to leave the subject of cooling water facilities without mentioning the need for the control of fouling by marine growths, both animal and vegetable. Under favourable conditions sea-weeds, molluscs, crustacea, and fish will all flourish in the open parts of a cooling system such as tanks and cooler boxes; and many are apparently capable of living also in total darkness, provided an adequate supply of oxygen is maintained.

These creatures are troublesome mainly when dislodged from their normal habitat, they cause choking

of heat exchangers and unit strainers, and the first step in their control is therefore the exclusion of adult specimens from the system by means of suitable mechanical screens at the pumphouse. Even so, a sufficient number of embryonic or adolescent specimens will get past the pumps to develop in the breeding places already mentioned unless checked by chemical dosage. Such dosage generally takes the form of chlorine injection at the primary pumphouse, the injection rate being controlled so as to maintain a

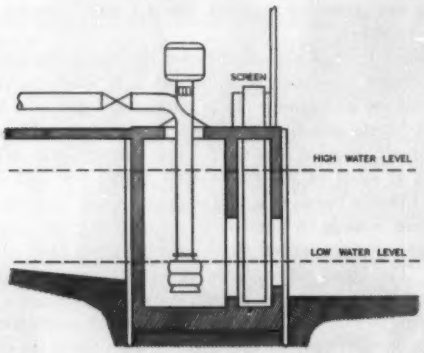

FIG 3 (*a*)
"WET" PUMPHOUSE WITH SUBMERGED VERTICAL PUMPS

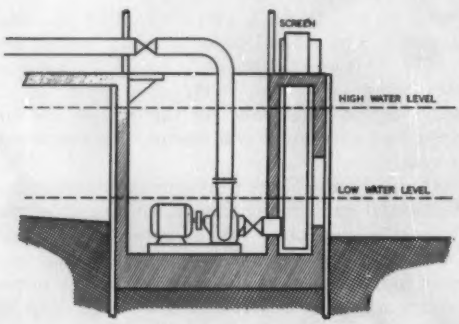

FIG 3 (*b*)
"DRY" PUMPHOUSE WITH HORIZONTAL SPLIT CASING PUMPS

residual of 0·5 p.p.m. in any tanks in which breeding or growth could take place. A point of special interest is that chlorine cannot be relied upon to eliminate barnacles which almost invariably attach themselves to parts of the system where there is sufficient turbulence to ensure them a copious food supply. These creatures appear to be capable of shutting themselves up for considerable periods when conditions are unacceptable to them and no economic dosage of chlorine seems to have any appreciable effect upon them. Their nuisance value, however, is confined to their tendency to puncture bituminous and certain other coatings and to the fact that if allowed to accumulate for very long periods they will increase the friction factor of the lines.

Boiler Feed

The make-up water for the refinery boilers may be derived from a number of different sources, such as municipal systems, privately owned water wells, nearby rivers, or from the refinery cooling water system itself if the water is of suitable quality. In all cases the water will require treatment for the removal of "hardness," and sometimes filtration or settling also will be necessary. There is available today a variety of treatment methods, all of which are capable of producing water of substantially zero hardness, and the particular method used will depend on the nature of the raw water. The detailed discussion of this subject is outside the scope of this paper, but it may be said in general that the designer of these facilities will have to choose a treatment capable not only of producing a water of zero hardness but also of reducing the dissolved solids and alkalinity to acceptable limits. Complete demineralization is the ideal, but this process is still extremely expensive, and its use is therefore likely to be confined to installations where the use of high-pressure boilers necessitates a feed of first quality or where the make-up rate is kept low.

Potable Water

The potable water requirements of a refinery, although small in relation to the total demand, are considerable when compared to those of a housing area of similar dimensions chiefly because of the large quantities of water that must be supplied to ships visiting the refinery marine terminal. It would be logical to make use of any adequate municipal supply which might exist in the vicinity of the refinery, since this would relieve the management of any anxiety concerning the quality of the drinking water at little or no extra cost. Where no local municipal supply exists or where the local supply is too small, it then becomes necessary to draw on refinery fresh water supplies. In such case, the water would require chlorination and possibly other treatment to render it fit for drinking, and the approval of the local Health Authority would have to be sought before such a step could be taken.

Compressed Air

The consumption of compressed air on a refinery may be broadly sub-divided under the headings "Instrument Air" and "Maintenance Air."

Apart from driving maintenance equipment, refinery maintenance air is also put to other uses, such as agitating tank contents for mixing purposes, flotation of heavier than water sludges, etc. In a typical refinery the demand for maintenance air, which is a fluctuating one, might be anything from three to five times that for instrument air. Apart from this the principal difference between the supplies lies in the fact that the "instrument air" which must be filtered and absolutely dry to avoid fouling and freezing is normally used at 50 p.s.i., whereas maintenance air is supplied direct from the compressors at about 100 p.s.i. Fig 4 shows a typical refinery air

system in which the 100 p.s.i. air from the compressors passes through an after cooler to the air receivers and thence out into the system. At a suitable point after the air receivers, a supply is taken off for the instrument air system. This air passes through, first, an oil removal trap, then one-half of a silica-gel drier to the instrument air mains, the pressure being reduced to 50 p.s.i. in a suitable valve after the drier. The two halves of the drier are used alternately on a timed cycle controlled by the automatic operation of two four-way valves, which admit heated regeneration air to one-half of the drier while the other is in use.

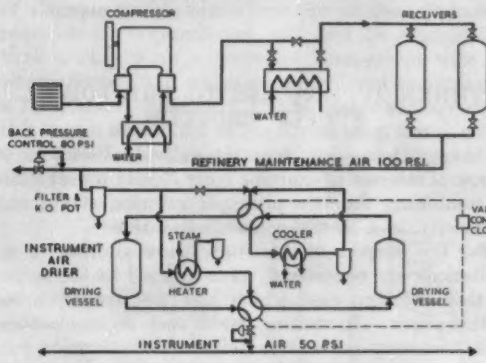

FIG 4

TYPICAL REFINERY COMPRESSED AIR SYSTEM

The spent regeneration air is cooled before being returned to the drier intake so that the entrained moisture may be condensed and trapped.

Devices of this kind will produce air dried below any dewpoint likely to be encountered in service, and will operate reliably for long periods without special maintenance.

Instrument air is one of the most critical utilities, in that a total failure of only short duration will affect all processes simultaneously, and could precipitate a major calamity. A total instrument air failure can be rendered extremely unlikely by the provision of both steam and electrically driven compressors and by ensuring that sufficient steam-driven compressors are always running to cover the possibility of an electrical failure. At times when for any reason it is inconvenient to base load the steam-driven compressors, the air receivers would provide sufficient capacity to safeguard the instrument air supply, while they are being started. It is necessary, however, to ensure that the receivers are not rapidly drained by heavy maintenance air demands, and to this end a back-pressure control valve is usually provided to throttle the 100 p.s.i. air supply when the pressure falls by a predetermined amount.

Both centrifugal and reciprocating compressors find application in oil refineries, the former generally for the larger installations. The first cost of centrifugal compressors is considerably higher than that of reciprocating compressors, and their principal advantage lies in the fact that they will operate for very long periods without maintenance. It is worthy of mention that the reciprocating compressor at its best is an extremely noisy machine, and while this may not, at first sight, appear to be a very serious disadvantage, it can result in a real nuisance where the installation is adjacent to offices or control rooms, for there seems to be no means of silencing the low frequency throb which emanates from reciprocating compressor air intakes.

At a cost of approx 3*d*. per 1000 standard cu. ft., compressed air represents a relatively expensive source of power for hand tools when compared with electricity. On refineries, however, it is almost exclusively used in preference to electricity for safety reasons, and it possesses at the same time the advantage of providing much more power in an appliance of given bulk and weight.

Except by elimination of leakage there is little scope for economy in the consumption of compressed air on a refinery, and the most serious cause of excess consumption is probably unauthorized use.

Refinery Fuel

There is at present a rapidly expanding market for various grades of fuel oil for supply to industrial consumers. On the other hand, refinery gas of average composition C_3 or lower has not as yet found any appreciable outlet as a product in the U.K., although the position is changing gradually as the Gas Boards become interested in such supplies, and refinery gases are already marketed in certain localities in the U.S.A.

Both gas and oil fuel are burned in the various furnaces of an oil refinery, and it is obvious from the foregoing that it is at present expedient to burn gas in preference to oil, and in any case gas is the preferable fuel, both from the point of view of operability and furnace maintenance. The gas production of a refinery fluctuates under normal conditions, and can be subject to almost total failure in the event of a process upset on the principal producing units. Because of this it is necessary to maintain a fuel oil system capable of supplying at short notice the entire heat requirement of all refinery furnaces. It is also necessary to have in operation at each furnace a minimum number of oil burners to ensure reliable ignition in the event of a gas failure, and it follows that the fuel gas and fuel oil systems must operate simultaneously and in sympathy with one another. Fig 5 illustrates one system by which this can be achieved. In this diagram the gas producers are shown discharging to the fuel gas main through a sulphur recovery plant wherein the H_2S content of the gas is reduced.

Consumers in the shape of various process and boiler furnaces draw their supplies from the fuel gas main, in which a substantially constant pressure is maintained by a pressure controller. Pressure in excess of the set pressure of this instrument results in gas being vented to the flare through a motor valve.

The flare also provides a disposal channel for gases emanating from the blowdown facilities and light slop storage during emergency conditions.

Fluctuations in the gas production are accommodated by automatic control of the secondary fuel supply, and in order that the process furnaces shall have the benefit of relatively steady operation this automaticity is generally confined to the steam plant, which will in any case be by far the largest fuel consumer. For this reason, a pressure controlled motor valve is installed in the gas supply line to the steam plant so arranged that it will throttle the supply to that consumer should the gas main pressure fall below the set pressure.

The steam plant fuel control or "fireman" valves are operated by the steam main pressure controller, and will therefore respond immediately to the

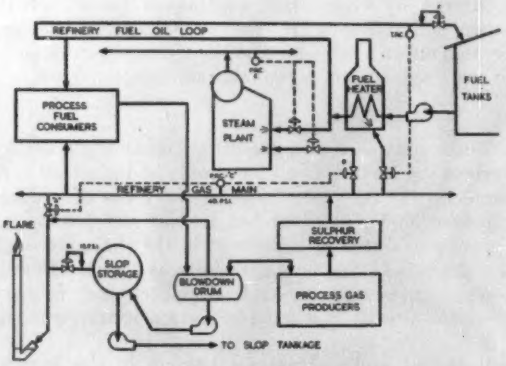

FIG 5

TYPICAL REFINERY FUEL SYSTEM

throttling of the gas supply by the introduction of more oil fuel.

From the foregoing it will be evident that substantial flaring should occur only when the gas production exceeds the combined utility and process demands.

Because fuel oil is a marketable product there is an incentive to burn in the refinery only the most viscous basic component undiluted by relatively costly blendstocks.

This basic component, generally atmospheric or vacuum pipestill bottoms, could have a viscosity of 1800 S.S.F. at 210° F and a pour point as high as 150°–200° F. In order to handle a fuel of this kind, it is necessary to heat it to some 450° F, at which temperature its kinematic viscosity would be about 20 cS, which is the normal viscosity required at steam atomizing burner tips. The fuel oil system shown consists of a fired heater through which the oil is pumped into a distribution loop. The pressure in this loop is determined by the setting of the recycle valve through which oil not burned by the consumers is returned to the storage tanks.

The distribution loop is insulated, but need not be heated, and an acceptable temperature at all points on the circuit is assured by maintaining a suitable recycle rate.

From the foregoing description of the fuel systems it will be evident that apart from any question of marketability, an economic incentive will exist for burning gas in preference to oil, in that both fuel for heating and steam for atomization must be consumed in order to make the fuel oil usable. This statement is true at present, but it is possible that future developments will open up such markets for gas as will completely reverse the position and make preferable the burning of heavy residues or even blended fuels, notwithstanding the extra charges associated with their use.

THREE APPROACHES TO THE POWER SUPPLY PROBLEM

Having discussed in turn the individual services, it is now of interest to examine more closely some effects of combining the two principal utilities, steam and electricity, in a central generating station.

For the purpose of this study three alternative installations are considered, each applied to the hypothetical refinery case which was postulated earlier in this paper. In making use of such an illustration, it is necessary to bear in mind that economic conditions obtaining in different parts of the world will favour different solutions.

In the U.S.A., for instance, the current trend in refinery utility installations is toward the elimination of the internal power station, and in certain cases, where the refinery can be located close to a suitable source, not only electric power but also steam is imported, liquid or gaseous fuel being supplied in return. In the U.K., on the other hand, and on the Continent of Europe, the majority of refineries have some form of power generating installation with or without a "grid" link.

The U.S. trend is primarily due to economic conditions peculiar to the U.S.A. There, petroleum derived fuels have entered further into the national economy than is the case anywhere else in the world, and because of this, there is a greater degree of integration between petroleum refiners, chemical manufacturers, and the power undertakings which have appeared in the form of privately owned utility supply companies wherever a sufficient concentration of industry exists.

It is obvious that a well run company equipped for no other purpose than the supply of steam and power would prove a rival with which no refinery utility installation could compete. When it is also realized that the capital saved by elimination of the refinery boilers and generators can be devoted to the purchase of productive plant it will seem surprising that so attractive a development has not yet taken place in Europe.

Many British and Continental refineries, situated as they are in undeveloped and sparsely populated

areas, do not offer so good a field for exploitation as do U.S. counterparts, and because these factors have so far excluded the separate utility company, refinery operated steam and power generating stations are economically attractive.

Since in the U.K. the Electricity Authority generates power by means of fully condensing turbines, there will be, all things equal, no incentive for the use of similar equipment within the refinery.

The generation of power by means of turbines whose exhausts will also supply the process steam is, however, highly advantageous.

In order to demonstrate these facts, Case No. 1, that of a simple installation where the whole of the power requirement is purchased, will first be examined so that it may form a basis for comparison with the alternatives, all of which are considered as applied to a 150,000 b.d. refinery. The utility flow diagram for this case is illustrated in Fig 6, and from this it will be seen that the boilers generate steam at 135 p.s.i. and 450° F.

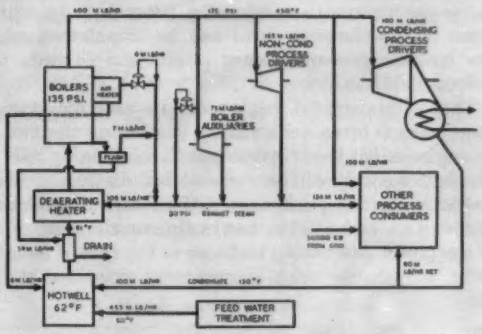

FIG 6

CASE 1. ALL ELECTRIC POWER PURCHASED

For the operation illustrated the total steam production is 600,000 lb/hr, consumed in the following manner :

Condensing process drivers	180,000 lb/hr
Non-condensing drivers including boiler auxiliaries	240,000 lb/hr
Process heating and other uses	180,000 lb/hr
20 p.s.i. exhaust steam for process and feed heating	240,000 lb/hr

The requirement of purchased electricity is 14,000 kW.

Under this design condition a very fair degree of balance exists between the LP steam consumption and production.

Other conditions can exist when the balance will be less perfect, and for this reason provision is made both for augmentation of the LP steam supply from the HP main in the event of a deficiency and for the disposal of any surplus which may exist after the feed heating requirements have been satisfied.

In order that the surplus LP steam may be disposed of without nuisance or waste, " gilled tube " air heaters are provided on the boilers in which this steam can be condensed. The " surplus " in the case illustrated would be little more than sufficient to heat the air to one boiler, but as already mentioned this is the design condition, and the primary function of these air heaters is to provide capacity for the absorption of greater surpluses under conditions of less perfect balance.

Turning now to the boiler feed system, it will be observed that there is a net condensate production of 100,000 lb/hr returned to the boiler hotwell, and after making due allowance for boiler blowdown and the feed heating contributions a treated water make up of 453,000 lb/hr is required.

This make up amounts to nearly 70 per cent of the total feed, but since the boilers are of relatively low pressure rating simple lime-soda or ion exchange treatment will suffice.

Use of the surplus LP steam in the feed heating deaerator achieves a feed temperature of 258° F.

The heat in the steam above feed temperature will, therefore, be 1024 B.t.u/lb, and assuming a boiler efficiency of 80 per cent a fuel equivalent of

$$(600{,}000 \times 1024 \times 100)/80 = 770 \times 106 \text{ B.t.u/hr}$$

will be required for steam raising.

It is now necessary to calculate the fuel equivalent of the purchased power, and since the fuel component of the cost per unit will be based upon the fuel consumed at the power station, it is necessary to take into consideration efficiency of generation.

The fuel equivalent of the 14,000 kW of purchased electricity therefore, assuming an overall efficiency of 25 per cent is—

$$(14{,}000 \times 3413 \times 100)/25 = 191 \times 10^6 \text{ B.t.u/hr}$$

so that the total fuel equivalent of the steam and power requirements in this case will be : 961×10^6 B.t.u/hr

or $(961 \times 10^6 \times 24)/150{,}000 =$ B.t.u/brl of crude throughput

In essence, therefore, the main characteristics of this system are simplicity and low capital outlay, and its efficiency may now be compared with the more elaborate and costly Case 2 and 3 installations, using the heat equivalent of the steam and power requirements as a basis.

Case 2, which is illustrated by Fig 7, consists of an identical refinery operation in which the whole of the electric power requirement is supplied by back-pressure turbo-generators fed with steam at 600 p.s.i. at 850° F from high-pressure boilers. The 135 p.s.i. process steam is supplied by the generator turbine exhausts, and has accordingly slightly more superheat than its equivalent in Case 1. Assuming that the turbo-generator has an overall efficiency of 67·5 per cent, $67{\cdot}5 \times (1432 - 1270)/100 = 109$ B.t.u. will be converted to power for every 1 lb of steam entering the turbine. This is equivalent to the generation of

about 32 kW/1000 lb of steam, and it will be evident that the Case 1 requirement of 600 M lb/hr process steam can be supplied only by generating a surplus of 5200 kW or by bleeding steam through the 600 — 135 p.s.i. by-pass which would be uneconomic. A state of approximate balance can, however, be restored if

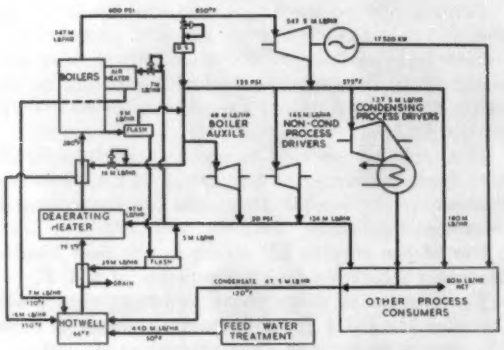

FIG 7

CASE 2. POWER GENERATED BY BACK-PRESSURE TURBINES

some of the condensing process drivers are replaced by electric drivers, and this condition, which is illustrated in Fig 7, will be the normal operation for which the installation is designed.

Any change in operation which brings about a change in the ratio of the process steam and power requirements will disturb the balance afresh and will necessitate either the disposal of surplus 135-p.s.i. steam or the "bleeding down" and desuperheating of 600-p.s.i. steam as the case may be. Provision for the disposal of surplus 135-p.s.i. steam up to a total of about 80 M lb/hr is made by means of high-pressure feed heaters which return condensate to the hotwell.

These heat exchangers will be oversized for normal operation and, like the air heaters, are regarded primarily as a means of absorbing surplus steam without waste.

Although the condensate from process sources has dwindled to a mere 8 per cent of the total feed in this case, there is a greater contribution from feed heating so that the treated water make-up remains around 70 per cent. In view, however, of the high pressure of generation, demineralization will be called for.

Since in this case the whole of the electricity is generated by the passage of some of the high-pressure steam through the back-pressure turbines, the heat equivalent of the steam and electricity requirements can be calculated in one step.

The feed temperature in this case has been increased to 280° F by the passage of surplus 135-p.s.i. steam through the high-pressure feed heater, and the heat in the 600-p.s.i. steam above feed temperature is therefore

$$1432 - 248 = 1184 \text{ B.t.u/lb}$$

If the boiler efficiency is assumed to be 80 per cent as before, the heat equivalent of the steam and electricity in this case will be:

$$547{,}000 \times 1184 \times 100 = 810 \times 10^6 \text{ B.t.u/hr}$$

$$\text{or } (810 \times 10^6 \times 24)/150{,}000 = 130{,}000 \text{ B.t.u/brl}$$

showing a saving of 24,000 B.t.u/brl over Case 1.

The use of back-pressure turbines for power generation represents the theoretical ideal, in that the energy waste associated with condensing the exhaust steam is avoided.

The principal limitation of such a system is its relative lack of flexibility, which necessitates the disposal of quantities of medium-pressure steam or the degrading of high-pressure steam during operations when the design state of balance is not achieved.

It is this feature which probably accounts for the rarity of back-pressure generation as the sole source of power supply in refinery installations. Where such an installation can be operated in parallel with the "grid" these objections are largely overcome, as is the case where back-pressure generators are operated in conjunction with condensing generators to which some of the electrical load can be transferred when the medium-pressure steam production exceeds the process demand.

The admixture of back-pressure and condensing generators is often achieved by combining the two in a single unit, the "pass out" turbine. Case 3, which is a study of this type of installation, is illustrated in Fig 8. As in Case 2 the steam is generated at 600 p.s.i. and 850° F, but in this case it is supplied to the power generating turbines at the rate of 590,000 lb/hr, the process steam requirement extracted at 135

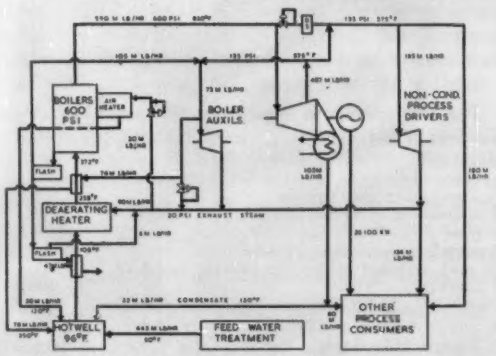

FIG 8

CASE 3. POWER GENERATED BY PASS OUT TURBINES

p.s.i. and 575° F, producing about 15,000 kW in its passage through the turbine. The total power demand has, however, risen to 26,100 kW, due to the electrification of the remaining process condensing drivers, and the balance of 11,000 kW is generated by the remaining 105,000 lb/hr steam passing through the LP end of the turbine to the condenser.

The condensate from process sources has diminished

due to the suppression of the condensing drivers, but the power turbine condenser makes a nearly equivalent contribution, and thanks to a greater recovery from feed heating the treated water make-up is about 70 per cent of the total feed, as in Case 2.

Pass out turbines can be so designed that any chosen power output can be developed when anything between 10 and 100 per cent of the total steam is being condensed. By varying the proportion of feed steam passing to the condenser, wide variations in the ratio of "pass out" steam and power production can be achieved, and these will accommodate any fluctuations in process steam demand which may occur from operational changes.

The pressure reducing valve and desuperheater between the 600- and 135-p.s.i. systems is therefore provided in this case to cover emergency conditions only, and the high-pressure feed heating system similar to that employed in Case 2 can now be loaded to the optimum extent, resulting in a final feed temperature of 327° F. The heat above feed water temperature is, therefore, 1432 — 340 = 1092 B.t.u/lb in this case and the heat equivalent of the steam and power

$$(590{,}000 \times 1092 \times 100)/80 = 807 \times 10^6 \text{ B.t.u/hr}$$

$$\text{or } (807 \times 10^6 \times 24)/150{,}000 = 129{,}500 \text{ B.t.u/brl}$$

The principal features of the three cases are set out for comparison in Table I, and it will be evident that the Case 3 installation consumes less fuel per barrel of refinery throughput than either of the other cases.

TABLE I

Heat-based Comparison of Cases

	Case 1	Case 2	Case 3
Total generated steam requirement, lb/hr	600,000	547,000	590,000
Total power requirement, kW	14,000	17,520	26,100
Process steam requirement, lb/hr	600,000	547,500	487,000
Hourly consumption of fuel equivalent for steam and power generation, B.t.u/hr	961×10^6	810×10^6	807×10^6
Heat equivalent of steam and power used, B.t.u/hr	662×10^6	639×10^6	563×10^6
Overall efficiency of steam and power generation, %	69	79	70
Consumption of fuel equivalent per barrel throughput, B.t.u.	154,000	130,000	129,500
Annual cash saving in fuel over Case 1 at £0·96/brl F.O.B.	—	£200,000	£204,000
Approximate percentage additional utility capital investment over Case 1, %	—	24	42
Approximate net cooling water saving over Case 1, I.G.P.H.	—	250,000	500,000

There is, however, little to choose between Case 2 and Case 3 in this respect, and both of the power generation cases show a fuel saving of about £200,000 a year over Case 1 with purchased power.

Further, no allowance has been made in respect of interest on borrowed capital or depreciation, or for cooling water requirements.

Incremental investment over Case 1 will be required for both Case 2 and Case 3 installations, and the approximate percentage increments are shown in the last column of Table I.

The use of actual investment figures has deliberately been avoided because for the purpose of such a hypothetical study as this they are apt to be somewhat meaningless.

The inclusion of investment charges would reverse the relative positions of Case 2 and Case 3, making Case 2 the more attractive, and by approximately doubling the cost of the purchased electricity in Case 1 would very greatly increase the incentive for internal power generation. As regards cooling water, because the condensing process drivers of Case 1 are backed out against electric motors in Cases 2 and 3, net water savings are achieved, which further add to the attractiveness of power generation.

There remains to be explained a seeming paradox, the fact that the Case 3 installation, which consumes less fuel per barrel than the others, has a thermal efficiency only slightly in excess of Case 1 and considerably less than that of Case 2.

The explanation lies in the fact that the efficiencies shown in this case are the overall efficiencies of steam and power generation, whereas the fuel requirement per barrel is dependent also upon the efficiency of steam and power utilization. In Case 3 more fuel is required to produce a given quantity of steam and power energy than in Case 2, but owing to the replacement of the process condensing turbines by more efficient electric motors a much smaller total quantity of energy is required to process a barrel of crude.

This revelation lays emphasis upon the principal limitation of the thermally efficient back-pressure system. Unless the steam demand can be maintained at a relatively high level in relation to the power requirement a workable state of balance cannot be achieved with back-pressure generators, and for a given process energy demand this places a definite upper limit upon the number of electric motors that can be used as drivers.

The occasional "bleeding down" of high-pressure steam is not a very serious disadvantage, but the problem of having to dispose of a large surplus of medium-pressure steam can be very real indeed.

The device of using the available capacity in a secondary feed heating system as a buffer on which to absorb the fluctuations in steam production is, so far as the writer is aware, untried, the more usual method of absorbing such fluctuations being by the provision of steam turbines as standby to some of the electric drivers. The latter arrangement is not a particularly convenient one, in that it generally places the control of this facility in hands other than those responsible for the operation of the utilities, though this would not be the case where a sufficient number of alternative drivers could be arranged on cooling water pumps or air compressors, all of which are normally under control of the Utilities Supervisor.

WHAT OF THE FUTURE?

It would be wrong to discuss the subject of utilities without indulging in some speculation as to the possible trend of future events. Steam, the principal

utility, is likely to remain as the most convenient means of transmitting controlled heat from one place to another. The larger steam turbines will, however, probably give way to gas turbines, particularly when the difficulties associated with the use of residual fuels in these prime movers have been overcome. The small non-condensing steam turbine will probably remain in the applications where it is used at present, because its choice for these duties arises from its reliability and convenience, which are unlikely to be surpassed.

A field in which steam is likely to be superseded by electricity is that of tank heating and line tracing, which duties can be performed superlatively and economically by the recently developed electrical heating cables. As these cables are developed for use with higher temperatures, they are likely to revolutionize also the refinery fuel oil systems by the elimination of costly fired furnaces, but in order to do this they will have to be made capable of operating for long periods at temperatures between 400° and 500° F.

Boiler systems are unlikely to change very much, although national economy drives may bring about the more widespread use of air heaters and economizers, which is at present avoided mainly because of the corrosion and fouling troubles associated with their use at part loads. It is also possible, although this is looking into the very far distant future, that atomic energy will replace fuel firing in the larger power or steam generating installations.

The electric motor will amost certainly hold its own in many fields because of its convenience and cheapness, but like the steam turbine, it may be ousted by the gas turbine for the very large installations, in which its advantages are less marked.

Another respect in which the utility scene is likely to change is in the field of instrumentation, where electricity will probably supersede compressed air to a great extent.

The tendency in the U.S.A. toward the elimination of the internal power station has been mentioned, and it is probable that the same trend will follow in the U.K. if future refineries and power stations are developed together in concentrated industrial areas.

DISCUSSION

J. O. Dugdale-Bradley: I am rather sorry that effluents were not touched on in the question of refinery utilities. In the paper Mr Shaw mentioned that effluents had been excluded. I had been looking forward to this point of great interest, which merits an entire paper; and which should be considered as an essential refinery utility.

Refinery utilities, or off-side facilities, represent a growing proportion of the projects they serve. One can build either a small refinery or a large process plant with capital investments of the order of £1½–3 million, whose off-site facilities and the utilities grouped together may represent capital of 1½ to 2 times that of the plant itself. Therefore, these points which have been brought forward by Mr Shaw are very pertinent because they bear on at least 50 per cent of the troubles associated with process plants during their life.

In the paper, steam-raising is considered as a fairly straightforward matter, but in fact it is becoming more and more complicated because the day has gone when one relied upon simple boilers without air heaters and economizers. My Company has been using air heaters in boiler plant to effect economy for several years. The complexity arising from their use is very small compared with the benefits obtained from their application. Economizers are also becoming more usual.

The question of the pressure at which steam is raised is important, particularly when one comes into the power generation field. My Company had a similar problem to that put forward by Mr Shaw involving alternators as shown and found very much the same answer. It is, however, thinking of installing boilers of 1500 p.s.i. pressure, which is high by refinery practice, but the benefits obtained from that high pressure, the efficiency gained, and the heat transfer level achieved, are well worth while providing they are coupled with power generation.

In the cases seen here which are based on a green-field site, steam and electricity are grouped together because they are interlinked, and the problems that arise when studying this type of arrangement are infinitely more complex when associated with running plants.

The problems my Company has studied are those involving the expansion of existing services, and it is believed that the back-pressure turbo alternator, as stated by Mr Shaw in his second case, is the answer. A degree of flexibility is obtained by running in parallel with the grid, and one does not have to rely upon "playing around" with surplus steam to achieve flexibility.

This is obtained by power generation, and its level is determined by the amount of low-pressure steam required. Low pressure is perhaps a misnomer, because one is dealing with a different range of pressures. My Company thinks of low in this instance as being 250 p.s.i., which is that of the normal process steam, and the pressure at which steam is raised in the present refinery utility boilers.

Taking into consideration the existing boilers, the refinery is in the happy position of having an extra degree of latitude in the overall scheme. Running in parallel with the grid, it is possible to generate or not, make low-pressure steam or not—it depends on the running of the back-pressure turbines. It is interesting to find that the result at which my Company has arrived is the same as that derived by Mr Shaw in that back-pressure generation is economical and in spite of a large capital investment in the high-pressure boilers and the associated equipment, one can show a pay-back in something like three years.

In the train of the high-pressure boiler come associated problems of feed water, because a much higher quality feed is essential, a demineralized water is necessary which adds to one's capital investment.

The actual sizes of the boilers mentioned in Mr Shaw's paper were of the order of 300,000–500,000 lb/hr. The 500,000 lb/hr size is on the high side, and my Company holds itself down unitwise to about 150,000 lb/hr.

Could Mr Shaw tell us his reason for setting his pressure at 600 p.s.i. when providing steam for back-pressure generation. In three cases, namely, 600, 900, and 1500, it was found that the limitation was the size of steam turbine driving the generator. One cannot use extra-high-pressure steam in a small turbine, because the blade height in the first stage becomes so short that the design will prove impracticable, and so the proposal is governed by that feature. In Mr Shaw's hypothetical refinery he handled a load of 14,000 kW, and that can involve

a sizeable turbine. The turbo alternator which my Company is at present considering is 10,000 kW, which is a somewhat larger unit than could be tolerated in such a refinery. Nevertheless, I would say that in the rating of his suggested refinery one should design for a pressure of between 900 and 1200 p.s.i. as one's initial steam-raising pressure, which again would show an increased efficiency over the 600 p.s.i. suggested. What therefore does Mr Shaw consider is the correct steam pressure level?

Associated with the boilers one has the boiler feed and the condensate to determine, and when using this very high quality water economics can go astray on the condensate return, because on previous ideas it might not pay one to recover the condensate. With the very high quality water needed it makes a different case, and pay-off can then be shown for extensive condensate collection systems in order to increase the percentage of one's condensate return, which, if one is lucky, in these days rises only to approx 50 per cent.

To provide adequate supplies of water is a problem which faces all refineries. The U.K. is known to be running short of fresh water, and industry all over the country is feeling "the pinch." In some ways, Mr Shaw's paper rather leant on the fact that one could have fresh water cooling, such as closed systems.

It is my Company's experience that fresh water cooling is opposed very much by the local authorities, because no matter what cooling towers one puts in, one cannot get below a 3 per cent loss on cooling, and that represents such a volume of fresh water that unless one is very lucky and is located at the side of a large river one is most unlikely to be able to obtain an adequate fresh water supply. This situation is becoming more and more difficult as the underground water supplies of the U.K. become depleted by the domestic consumer to a greater degree than previously was considered possible, and one should ignore fresh water cooling at this stage and concentrate on salt water. There is quite a lot of work now being done on the desalting of brackish waters. I would like to ask Mr Shaw if he has had any experience in dealing with this aspect of utilities, because unless something is done within the next three to five years in producing in an economic way artificially desalted water, one will have to go much more into the use of salt water for cooling purposes. It is impossible to use saline waters for most process water or for boiler feed, but the economics of a steam raising system might be governed ultimately by the ability to obtain suitable water for boilers and the extent of the condensate return. Even the major U.S. refineries, which are Mid-Continent, have to locate themselves on the Mississippi or somewhere like that in order to get adequate supplies of suitable water. The method of electrodialysis which is being developed provides a way of desalting water to a state which would even make it good or potable. The process is known to have low operating costs. It is also known at the present time to have very high initial capital costs, and unless and until these capital costs come down to a lower level one cannot talk confidently about fresh water cooling. I would like to ask Mr Shaw if his Company have had a survey on the methods of desalting water.

Another source of water which has not been tapped in the U.K., and which my Company is investigating at the moment, is the use of sewage effluents. The domestic water which is coming as effluents from big industrial concerns if often perfectly suitable for process water and boiler feed water after adequate treatment.

I appreciate that trouble is being experienced with the detergents in these effluents, but that source of water is not sufficiently recognized, and when one considers that in Germany the water flowing down the Rhine from Basle to the mouth goes through the natural cycle twelve or thirteen times, it is apparent that there is a potential supply of fresh water in sewage effluent. This could be tapped if one took the trouble and spent the money to put in the filtration and treating equipment. I would like to ask Mr Shaw if that potential has ever been studied. My Company is at the present time studying it as a possible source for fresh and process water, it is quite a complicated process, involving not only the normal filtration beds but also considerable after-cleaning. However, the capital outlay may be worth while.

One of the points that Mr Shaw raised in his paper was on electric heating for pipelines using cables. He advocated such equipment, and I was surprised because my Company has tried it in small bitumen tanks and while it is very convenient for general application over wide areas, I consider electric cable heating to be very expensive both in capital and in running costs. Perhaps Mr Shaw would give us a little more information on this subject, because it is of considerable interest if one can economically heat by electricity.

There are two more points I would like to raise: the use of gas for fuel and the application of atomic power.

Gas as a fuel is comparatively wasteful, it is being found more and more with the development of chemicals that refinery gas is too valuable to be burned. It becomes, in fact, the charging stock for a whole range of chemical products, and therefore one is tending to avoid taking gas into consideration as a fuel because of this better alternative. The gas turbine as a prime mover has not been mentioned, but it might come into its own in the future for large units in a refinery. Its use will depend in the development of the gas turbine and the availability of gaseous fuel.

I would like to ask whether Mr Shaw thinks atomic power will become available in such small and economic packs that one can use it for steam raising on the units in refineries, *e.g.* 200,000 lb/hr.

My Company is not certain how far it can extend its condensate collection facilities economically with the scheme it has at present using 10,000-kW back-pressure turbines. At the present time 50 per cent probably represents an attainable figure.

J. A. Shaw: I, too, am sorry that I was unable to include a section concerning effluent systems, which are a very costly part of the utilities of a refinery. A paper of this kind has to cover an enormous field, and if the component subjects are to be satisfactorily dealt with, it is difficult to keep the length within reasonable limits. It is for this reason I have reluctantly omitted a discussion of effluent systems, which, as Mr Dugdale-Bradley has said, is a subject that merits a paper of its own.

I was interested to hear that Mr Dugdale-Bradley uses and advocates both air heaters and economizers in the utility installations with which he is concerned, also that he is contemplating the use of boilers of 1500 p.s.i. rating. I would have thought that boilers of such a pressure could be contemplated only for what would eventually be a fairly large generating installation and for one in which the whole of the power generating steam is condensed and returned to the feed system.

However, Mr Dugdale-Bradley's statement that he shares my preference for back-pressure turbines suggests that some of the process steam is to be taken from the generating turbines exhausts. Am I right?

J. O. Dugdale-Bradley: In the present scheme, the position is that with 10,000-kW turbines it is not certain how far one can make an economic condensate return. But probably only approx 50 per cent of the steam raised will turn to condensate. Having been through the turbine, the steam is then distributed in exactly the normal way of refinery processed steam, with all the associated difficulties of getting it back to the boiler house as oil feed condensate.

J. A. Shaw : The paper states that the inherent lack of flexibility of the back-pressure turbine could be countered by running it in parallel with the grid. That is undoubtedly one solution to the problem, but to get the maximum benefit from the use of back-pressure turbines, it is necessary to back out all purchased electricity, which compares so unfavourably in cost with that which can be produced in a suitable refinery power station.

This and other remarks I have made may give the impression that I have my knife in the C.E.A.

The point I wish to make is this. If the C.E.A. are to remain competitive as suppliers of industry, they will have to find a market for the vast quantity of heat which at present passes into rivers, estuaries, or to the atmosphere in their condenser cooling water. If the utilization of this heat could be realized, the cost of electricity to all consumers and, incidentally, the nations fuel bill, could be drastically reduced.

Mr Dugdale-Bradley asks why I chose a pressure of 600 p.s.i. for power generation.

First, I am considering fairly small installations—the turbines of Cases 2 and 3 would be about 7·5 MW units—and I would have thought that a pressure of 600 p.s.i. would be just about the optimum for machines of that size. I agree that there are benefits to be obtained from the use of high pressure and/or temperatures, but I should have thought that the mechanical design considerations to which Mr Dugdale-Bradley has himself referred would set the pressure limit for a 7·5-MW turbine rather lower than 900 p.s.i. There is too, the fact that, whereas a temperature increase affects only the superheater, high-pressure piping, and the turbine h.p. end, a high operating pressure affects every part of the boiler, its auxiliaries, the turbine, and the feed water treatment, and brings in its train greatly increased capital expenditure.

There is also the question of fuel. Refinery utilities must operate on any fuel that may be available and upon that which is currently the least marketable. The operation of high-pressure boilers upon the less acceptable fuels may possibly court vanadium corrosion in hot places.

Another factor which influenced me in my choice of operating pressure was water treatment. With a pressure of 600 p.s.i. it might just be possible, given a suitable raw water, to get away with normal ion exchange water treatment, whereas for higher pressures demineralization and silica removal would be obligatory.

Demineralization units supplying the small make up to fully condensing power stations are commonplace, but demineralization of the considerable raw water requirement of refinery utilities is a step that would need careful consideration.

On the question of the desalting of brackish waters, I regret that I cannot help very much. My Company has given no serious consideration to this process, possibly because Fawley is relatively fortunate as regards fresh water supplies. I understand our American affiliates have investigated these processes, and I believe the capital cost works out at about $1/U.S.G/day. The operating costs appear to be in the region of 4*s*. 0*d*. per 1000 gal, which I would not call low. I do not know what else, if anything, must be done to desalted water to render it suitable for boiler feed. At Fawley, salt water is used for cooling, and consideration has been given to the use of salt water recirculatory cooling towers as a means of reducing expansion costs. I understand that while no manufacturer has so far made a salt water cooling tower of any size, both the Marley and Fluor companies consider it to be a practical proposition.

The use of sewage effluent for boiler feed has also received passing consideration at Fawley, but was abandoned because the quantity of the available effluent was insignificant in relation to boiler feed requirement. I can see no reason why a detergent-free sewage effluent should not be used for boiler feed after suitable filtration and treatment, although the chloride content of such effluents can be on the high side and chlorides are not removed by treatments other than demineralization. Some detergents defy removal by any known means, and if left in would certainly give rise to foaming in the boilers.

On the electrical heating of pipelines, I have not perhaps made myself quite clear. Such systems are economically attractive both as regards capital and operating costs :

> (*a*) For fuel oil systems where they compete with a fired furnace and a loop system in which the oil must be circulated at high temperature.
>
> (*b* For very long pipelines where a number of intermediate boiler stations is required to supply the tracing steam.

Other advantages are that they can provide temperatures outside the scope of normal process steam heating and that they are easily controlled thermostatically, so that heat is applied only when and where it is required. For such applications as the heating of small tanks I would not expect them to compare favourably with steam.

In the paper I mentioned the possible future use of gas turbines as prime movers, particularly in place of very large condensing turbines or electric drivers.

Both Mr Dugdale-Bradley and myself have forecast that gas production of refineries is likely to be taken up in the future by the development of new markets and chemical projects, and the future of the gas turbine would therefore seem to depend to a large extent upon its ability to tolerate residual oil fuels and, in particular, vanadium-containing fuels, and this is a field which is currently being subjected to intensive research.

On the question of atomic power I can be of little help. I suppose there is no reason why it should not find its way into the larger refinery power stations, but on the whole I cannot believe that its future lies in the field of refinery utilities.

J. O. Dugdale-Bradley : I would like to answer one or two questions put by Mr Shaw. First, my Company is aiming to use residual fuels in 1500-lb boilers. I cannot say that this has succeeded because it has not been tried out for high-pressure work.

As regards demineralization, one point that perhaps I did not emphasize was that one is dealing with an oil and chemical works, and therefore it is highly probable that a certain amount of demineralized water will be required for process purposes. I cannot state the exact size of the demineralizing plant, but the two 60-ton boilers will require fully demineralized water. It will be something of the order of 30,000 gal/hr of demineralized water. The total dissolved solids of this water are down to less than 0·5 p.p.m., the silica content will be less than 0·05 p.p.m., and the conductivity 0·5 reciprocal ohms at 20° C.

As regards effluents, in the case I mentioned under investigation, it involved a quantity of approx 250,000 gal/day, which is quite a considerable amount of fresh water.

I was interested in Mr Shaw's remarks on electrical heating, and it appears it is worth while making a further examination of this idea.

R. B. Besley : I was rather surprised to see in the preprint that Mr Shaw makes reference to steam atomization of fuels which, I assume, refers not only to his utility boilers, but also to refinery plant furnaces.

In the organization with which I am associated a pressure atomization system is employed almost ex-

clusively, and steam atomization is reserved for very minor applications only. Steam atomization is considered to be out of date and economically inefficient, and I should like to assure the author that the pressure-return atomization system gives eminent satisfaction, even when burning the 300 Penetration residual fuels (30 cS at 375° F) which form the majority of the overall refinery fuels. I admit that the temperature and viscosity range over which pressure atomization is accurate and efficient is more restricted than with steam atomization, but with automatic control, good design, adequate lagging, and speed of circulation, there has been little operational trouble.

J. A. Shaw : I am very interested to hear that there are refineries in which pressure atomizing burners are used, and particularly that they are satisfactory on residual fuels. Do I understand that you used such fuels as pipe still bottoms in your burners? (Answer by Mr Besley : 300 penetration asphalt.)

I suppose there are obvious advantages in the use of the pressure jet burner, in that it is not necessary to spend so much money in utilizing the fuel, but its chief limitation is its lack of flexibility—it cannot cope with widely varying outputs, and I believe that was the chief reason for its absence in the majority of refineries. I can see no reason why the pressure jet burner should not be used on very many process furnaces where fairly steady operation can be expected, but I would have thought that for the steam plants, which must be capable of coping with enormous load increases at a moment's notice and where a considerable range of fuels must be burned, the steam atomizing burner would remain supreme.

I was at some pains to emphasize that as far as the steam installations were concerned, one should play safe above all else. I hope, in doing so, I have not offended some people by making it appear that economy is of no importance in the utilities. I merely wish to say that considerations of economy are very definitely secondary to those of reliability and safety as far as the steam raising installations are concerned, this factor will, I believe, weigh in favour of steam atomizing burners.

D. Webster : In the case of power generation I note a large capital expenditure for the saving of £4000 p.a. in fuel, which brings me to my point regarding economizers. Had Mr Shaw " fitted " an economizer to his boilers, then the saving would have been at least £15,000 p.a. I have used economizers on refinery boilers for some years now, and before coming to this meeting I looked up their record. They were installed in 1936, *i.e.* twenty years ago—and it has been necessary to replace only one element. That is, one element in five boilers, and this was not the fault of the economizer but was owing to faulty operation. Mr Shaw's boiler efficiency of 80 per cent surprised me, and it was this figure which directed my attention to the remarks regarding the reliability of economizers. In Mr Shaw's hypothetical refinery would it not be easier to save money at the boiler house end rather than the power generation end.

The statement that refinery loads are widely varying puzzles me. I presume that Mr Shaw's refinery operates 24 hr/day and 7 days per week. I find that the refinery load varies by a maximum of about 10 per cent, unless there is a major shutdown, when there is prior warning, in which case it is a simple matter to take a boiler off line. Pressure-jet atomizers are employed and these take care of any load variations very well.

Another point is the question of cast iron *v.* lined steel piping for salt water mains. It appears that everybody is chasing around to find some fancy lining for steel pipe in order to avoid using cast iron.

I have two cast iron mains under my control which are over thirty years old. They occasionally become internally coated with barnacles and mussels, but these are removed by various treatments, and the lines never give any trouble. I know, however, of bitumen-lined steel lines which have failed after only three years, maybe due to the lining being pierced by barnacles, but I doubt it, because we have not noted any barnacles in those lines.

I was interested to hear that although the author uses chlorine treatment, it is not entirely effective in dealing with barnacles and mussels. My Company uses copper sulphate and finds it quite effective and cheaper. Certainly, with regard to mussels, copper sulphate is effective, but it is only effective if it is injected in slug doses. It appears that mussels may be able to acclimatize themselves to this treatment, and unless intermittent dosing is resorted to, then they may come to regard it as a special sea-food!

J. A. Shaw : It has been my experience that air heaters, at all events, are exceedingly troublesome in refinery boilers, because the fuels that one uses in them are from time to time relatively sulphurous. I am interested to hear that one can have fairly trouble-free performance from economizers under these conditions, and I should be interested to know more of the circumstances in which they are used. Some boilers at Fawley are fitted with cast iron economizers, but even these, if not very troublesome, are certainly the most troublesome part of the boilers to which they are fitted.

My experience with air heaters on refinery boilers has been wholly bad, and they are better not used.

I agree that one could save a lot of money by the use of these devices, and I think that in the future, when all the customary fuels are taken up for making chemicals and that sort of thing, one will probably have to face up to the problem and find some way of employing them.

At the present time, I suggest that the incentive is not really great enough to drive one to this length.

Reverting to the question of my economics and the savings attributable to the use of economizers, I would point out that the capital differential between Cases 2 and 3 is not directed particularly toward the saving of £4000 p.a. in fuel, which is incidental. The point I wished to make was that fuel savings of the order of £200,000 p.a. could be achieved by the interr al generation of power, and while the fuel economy of all three cases could undoubtedly be increased by the introduction of economizers, this is a side issue.

In actual fact Case 2 becomes outstandingly the most attractive if the investment charges are taken into account. The gross annual savings over Cases 1 and 2 then being about £270,000 and £100,000, respectively.

The kind of load variations to which I was referring are those resulting from refinery upsets, which can be very great. It is not at all unusual to have a call for an extra 100,000 lb/hr of steam more or less immediately, to accommodate, for example, a blower failure on a large catalytic cracking unit.

In regard to cast iron piping, this, notwithstanding its very high cost, is probably more widely used than any other type. Its cost, which is twice as much as steel or bitumen-lined steel piping, is, however, its principal disadvantage. Cast iron piping is otherwise extremely satisfactory, and it has the great advantage that it can be buried in the ground without special protection and yet have a long life.

It has been my experience, and I have the confirmation of others who have studied this subject, that barnacles are, for all intents and purposes, resistant to chlorine, but I do not mean to imply that they cannot be killed by giving them enough chlorine or that any economic dosage does not seem to have a great deal of effect on them once they are established. There are still barnacles in certain places in the water system at

Fawley, notwithstanding quite heavy periodical doses of chlorine, and the shock treatment to which Mr Webster referred has not been effective in clearing them out. Mussels, on the other hand, appear to succumb to shock treatment; in fact, I have the impression that they are fairly easily killed by chlorine. Mussels are curious things in any case. They will change their habitat from time to time simply because of some apparently quite minor pollution of the water in that neighbourhood, so it is understandable that they would succumb to dosage by chlorine.

I was very interested to hear that copper sulphate had been found effective in tackling barnacles. I should like to know what sort of concentrations are necessary for it to be effective, and how are such doses determined? In the case of chlorine, the criterion appears to be to maintain a residual of $\frac{1}{2}$ p.p.m. in the extremities of the system, such as tanks where marine organisms can collect.

D. Webster: My Company's economizers have been in use on a wide variety of fuels, ranging from coal-tar pitch during the war years to residual fuel, and for some years neat unneutralized acid sludge has been burned. That is about the hardest treatment one can think up for any economizer.

Regarding the copper sulphate dosage, this is applied at the rate of 10 p.p.m. every other day for a 2-hr period. It is injected only when the sea temperature is above 50° F, because below this temperature the mussels stop breeding, and if they are kept out in the summer and do not breed in the winter, then there is no point in wasting sulphate.

E. Bonwitt: May I ask what trouble the author has experienced or expects when burning residual fuels? I assume that the paper refers mainly to economizer blockage. This could be caused in two ways, and both need not necessarily occur. One difficulty is that the combustion is incomplete, which may cause fuel particles to deposit on the economizer; this should be avoided by improving combustion. The other difficulty, which is very widespread, is caused by deposits of alkaline sulphate on the economizer. This is formed from SO_3, which the combustion of many residual fuels produces. The layer of sulphate is usually sticky, and may cause rapidly growing deposits of ashes and soot. As these sulphates are easily soluble in water, this type of deposit can be removed by water washing. This is done regularly with the boilers in operation, and is, in fact, the only way by which it was found possible to keep the boilers on line for long periods.

Another question is in connexion with electric heating. The paper refers mainly to electric heating of fuel oil in tanks. Has the author had experience with electric tracing of pipelines? Electric heating cables are used by my Company in non-hazardous areas and for moderate temperatures. Is it a practice at Fawley to use such cables in hazardous areas? I feel that this is somewhat risky. Although the maximum surface temperature of the cable can be limited by proper design, a break is always possible or the metal sheath can be damaged mechanically or by chemical attack.

J. A. Shaw: The trouble to which I referred in connexion with the use of economizers in refinery boilers was primarily that of corrosion. Mr Bonwitt has also mentioned the question of sticky deposits forming on economizers during periods of imperfect combustion, and at Fawley this trouble has not been encountered, chiefly because the economizers are of a type which do not clog easily. My experience of the use of economizers in refineries is, however, confined to the two very small boilers at Fawley in which the troubles have been purely of corrosion, although the economizer tubes in question are made of cast iron.

The deposition of sticky sulphurous deposits is very troublesome in air heaters, particularly the kind of air heaters where the flue gases pass through the tubes and the air outside the tubes. At Fawley it has been found that air heaters of this kind become completely choked in a very short space of time. In fact, I have known cases where such air heaters had to be cleaned out at three-monthly intervals because they restrict breathing of the boilers seriously if left any longer. Severe corrosion of the air heater tubes was also experienced. All this seems to suggest that the combustion conditions are imperfect. On refineries, particularly where a variety of fuels must be burned and where more than one fuel must frequently be burned at one time in the same furnace, it is extremely difficult, even with automatic aids, to maintain combustion efficiency at the level necessary to ensure freedom from trouble with economizers and air heaters. That really is the reason for my dislike of these devices.

On the question of electric heating, the installation to which I referred is, in fact, a line tracing installation. It was intended to use electric heating for a fuel oil system, in which the fuel would be supplied from the source (in this case a pipe still) at a sufficiently high temperature for immediate use, and one was merely going to trace the piece of line which carried it to the consumers with suitable electrical cable, connected up sectionally, and thermostatically controlled in sections, so that if at any place the temperature fell to a dangerously low level, that section of heating cable would cut in and supply the necessary heat boost. I have no experience of the use of these cables for heating tanks, although there are now one or two types of cable which are suitable for that purpose. Electric heating cables can be used for internal line tracing or direct heating of hydrocarbon fluid, *e.g.* in a tank, and used in that way, I should think they would be very satisfactory and efficient. There are no qualms about using these cables in hazardous areas in the refinery. They are tremendously robust, and one can subject them to severe treatment without any mishap occurring. They can be hammered flat without a failure taking place, and they are extremely difficult to break or cut. The dangers associated with their use need not be any greater than those with many other types of electrical equipment which are of necessity used in a refinery.

W. S. Morris: Dealing first with the application of heating cable for tracing purposes, I would issue a word of caution in respect of copper-sheathed cables, as the sheath may not have a very long life in certain areas of refineries handling Middle East crudes. I know of instances where copper air lines associated with instrumentation have had to be replaced within a comparatively short time as the result of exposure to sulphurous atmospheres.

In regard to the electrical aspects of the paper, the author mentioned a figure of 2 kW-hr for processing each barrel of crude oil. I find that figure a little low compared with the usual one of 3 kW-hr. For a highly integrated refinery, having large lubricating oil process facilities and a chemical plant, the figure can rise up to approx 4·5. As a point of interest the kilowatt maximum demand of a refinery can be roughly assessed if the crude intake in tons per day is known—the two values are almost identical for the hypothetical project put forward by the author.

The author refers to the ring main system as being the common method of distribution in the U.K. That may be true of other industries, but as far as the petroleum refining industry is concerned, the radial system predominates.

The general method of distribution put forward by the author is in the main identical to that used in refineries

with which I am associated, but we do not use automatic bus ties. I am surprised to note from Fig 2 that an 11-kV cable is apparently solidly connected to another cable, presumably by an underground T-joint. I would not advocate such a practice on 11-kV feeders, particularly for one between an intake and a main substation. The presence of a T-joint must constitute some degree of weakness, further in the event of a fault, then the existence of a branch cable makes location much more difficult. The extra cost for providing separate feeders from either the intake or main substations is well worth while in such cases.

In my organization the primary distribution is 6600 V, which is also the supply voltage for motors of 250 h.p. and above.

As far as automatic bus ties are concerned, these are warranted only if frequent failures of the outside supply are expected. Complicated control equipment is necessary to ensure that the change-over operations take place only when the situation demands and not under transient or some other fault conditions, such as a bus bar fault, when it would be advantageous not to have any change-over operation at all.

The change-over equipment must be tested periodically, and the arranging of such tests without prejudicing the operations of process units can also cause difficulties. It would be interesting if the author would enlarge on his experience with the automatic bus ties and confirm that supply conditions generally have warranted their installation.

In very much the same connexion, it is noted that all motors are fitted with under-voltage trip delays and that it is usual for all but the largest motors to stay on line during automatic change-overs. The largest motors in a process unit are usually the charge pump drivers, and surely these are the motors which should be kept on line all the time! Our practice is to apply delayed under-voltage tripping only to key motors, so that in the event of a transient, the motors of lesser importance are jettisoned fairly quickly, and this allows the supply system to recover in the minimum time.

I fully agree with the author's comments in respect of synchronous motors, but a further objection to their use, at least in dangerous areas, is the difficulty of ensuring the necessary degree of safety, particularly of such things as slip rings and exciter commutators. Notwithstanding, there is probably a case for the use of synchronous induction motors, at least in safe areas, as while they may pull out of step during a transient, they will continue to keep running as induction motors.

Static condensers can be added fairly cheaply to improve the power factor, and particularly so in the case of a refinery, as the inherently high load factor does not demand the use of extensive automatic devices to switch the condensers in and out of service to compensate for load changes. Our own practice is to connect static condensers in units of up to 100 kVA to the 415-V load centres, as in this position they tend to improve the voltage regulation throughout the system, as well as having the desired effect at the main metering point.

J. A. Shaw: I am interested in Mr Morris' experience of corrosion of copper air lines, as these were considered when contemplating the use of an electrical heating system at Fawley. For this purpose the copper-sheathed cable has an insufficiently high temperature rating, and it was thought that steel-sheathed cable would not be subject, or so subject, to that type of attack. One refinery installation of copper-sheathed cable in the U.K. where some flooding was experienced suffered very serious electrolytical attack owing to the copper cable being in contact with a steel pipe in the presence of salt water.

I am also very interested in Mr Morris' remark about the method of getting the kW maximum demand of a refinery, and I accept his criticism of my figures, but he will appreciate that the electrical load will vary considerably from installation to installation. I would have thought that in refineries where electric power was purchased, it would not have been as high as the figure he mentioned, but it obviously depends very much upon the type of drivers selected for the various items of equipment.

I have not given any thought to T-joints on 11-kV feeders, but I agree with Mr Morris that this is possibly not the best practice nor a typical arrangement in the U.K.

Automatic bus ties, on the other hand, are most definitely warranted. At the present moment at Fawley one has to contend with rather peculiar supply conditions in that the refinery is fed from a distant substation by two feeders which are carried on the same line of poles. The bus ties have worked and have overcome serious trouble on more than one occasion. I agree that they need careful and constant maintenance, and there is also justification for a remote indicating system so that a faulty bus tie can be speedily located and adjusted in an emergency.

There are very large process electrical drivers at Fawley. The only large electrical drivers are utilities, the salt water pumps, and a compressor, and one accepts that these come off the line if there is an automatic change-over. They can be started very quickly, and since one has, in the case of the cooling water, one of those systems in which there are tanks in between the primary pumping source and the refinery, a momentary interruption is of no consequence. There is also a steam-driven compressor which is normally kept running to cover the effect of an electrical failure on the air supply.

J. Thurley: I would like to ask Mr Shaw for further details of the method of chlorination used at Fawley.

My Company chlorinates salt water for fouling prevention in the cooling system, and in the initial phase of the operations some difficulty was experienced in obtaining sufficient chlorine residual. Therefore full 24-hr surveys on chlorine demand of Thames water for different seasons of the year were carried out, and the chlorine demand was found to vary from 3 p.p.m. at high tide to 16 p.p.m. at low tide. The high demand was apparently owing to polluted river water flowing down stream with the change in tide, and containing sewage and trade effluents.

As a result of the surveys it was decided to inject (*a*) during the summer for 1-hr periods 2½ hr before high tide with another 1-hr period 1 hr after high tide, and (*b*) during the winter for a 1-hr period at every high tide. A chlorine dosage of approx 7 p.p.m. is carried out in order to give a residual of 2–3 p.p.m. at the water intake.

No evidence of slime formation or barnacle fouling has been observed, but mussel fouling was present in the cooling water lines. It was found that once adult mussels were present in the cooling water system it was difficult to remove them with intermittent chlorination. A literature survey has shown that mussels, once they have formed their bivalve shells, can be killed only by continuous chlorination, a chlorine residual of 0·5 p.p.m. being sufficient.

Do you find it necessary to supplement your intermittent chlorination by a period of continual chlorination, for instance, 5–7 days?

J. A. Shaw: At Fawley chlorine is injected at the rate of 7 p.p.m. for 1 hr each day and for a continuous period of 7 days in each month. The system consists of salt water pumps which draw water from Southampton Water, and pump it up into tanks situated near the refinery from which the secondary pumps take their suction. The chlorination schedule is based on an attempt to obtain a 0·5 p.p.m. residual in those tanks.

It has been found that any attempt to obtain a residual farther on in the system than that, after it has been through process units, is hopeless.

The principal trouble experienced at Fawley is that of marine organisms developing in the tanks to a stage at which they can withstand the daily dose of chlorine. Their subsequent destruction then results in their being washed through in large quantities, causing the choking of heat exchangers, etc.

The chlorination procedure outlined above has proved effective in preventing this occurrence, but has, I repeat, little or no effect upon the barnacles, which are to be found in considerable numbers on the walls of the tanks and at bends in the pipelines.

Their absence from straight lengths of pipe is presumably because the stagnant boundary layer along the pipe wall either hinders the attachment of the embryo or denies them an adequate food supply during their early growth.

The meeting then closed with a unanimous vote of thanks to the author.

PLATFORMING OF PARAFFIN WAX*

By P. SCHENK,† A. B. H. VERVOORN,† H. I. WATERMAN† (Hon. Fellow), and A. B. R. WEBER†

SUMMARY

Paraffin wax (average molecular weight 375) was vaporized with hydrogen and contacted with a supported platinum catalyst at 0·7–1·0 *WHSV*, 410°–450° C, 30–100 atm, and molar ratios (H_2/wax) 55–185.

It appeared that three reactions occur, namely isomerization (branching), hydrocracking, and, to a minor extent, cyclization. The degree of cracking was derived from distillation curves. The degree of branching in hydrogenated distillation fractions was determined according to the specific refraction–specific parachor method, which was adjusted beforehand to 70° C and the mean total number of rings per molecule in the fractions was determined according to the *n–d–M* method.

From the experimental results it appeared that higher reaction temperatures favour all three reactions, while these reactions are suppressed at higher molar ratios H_2/wax. An increase of contact time has little effect on isomerization, while hydrocracking and cyclization become more pronounced.

In order to select optimum isomerization conditions a quantitative comparison was made of the degree of branching in the reaction products. Considering an input of 100 gram atoms carbon (1410 g wax) it was found that under optimum conditions about 10 gram atoms tertiary carbon are present in the molecular weight range 300–400. In these cases hydrocracking was limited to below 20 per cent.

PART I. DETERMINATION OF THE AVERAGE NUMBER OF BRANCHINGS PER MOLECULE IN SATURATED HYDROCARBON MIXTURES

INTRODUCTION

LORENTZ [1] and Lorenz [2] defined the molecular refraction as

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

where n = refractive index, usually measured at 20° C for the sodium-D-line;
d = density of the liquid at the same temperature (grams/ml);
M = molecular weight.

According to Lorentz and Lorenz, the molecular refraction is an additive atomic function, *i.e.* its value can be derived from the molecular structure by summation of the atomic refractions. Furthermore, this function was considered as independent of temperature. The molecular refraction of normal alkanes and *n*-alkyl*cyclo*hexanes at 70° C is, however, higher than at 20° C.

Sugden [3] introduced the molecular parachor

$$P = \frac{\sigma^{\frac{1}{4}}}{d - D} \cdot M$$

where σ = surface tension (dynes/cm);
d = density of the liquid, measured at the same temperature as the surface tension;
D = density of the vapour in equilibrium with the liquid under the conditions of measurement;
M = molecular weight.

For the *n*-alkanes at 20° C the value of D may be neglected from *n*-nonane upwards; at 70° C D may be neglected from *n*-undecane upwards. According to Sugden, the molecular parachor is almost independent of temperature and is an approximately additive function. From this paper it will appear, however, that the molecular parachor of *n*-alkanes from *n*-undecane at 70° C is higher than at 20° C and that the temperature influence increases at higher molecular weights. Mumford and Phillips [4] investigated the additivity of the parachor function and showed that the parachor was not a simple additive function, but that it was susceptible to changes in structure. They evaluated the influence of chain branching and proposed a negative correction to be applied for each branching in a chain.

Waterman and Leendertse [5] based their method on the following starting points:

(1) The experimental fact, that the molecular parachor of saturated hydrocarbons depends on their degree of branching.

(2) The assumption that the molecular refraction of saturated hydrocarbons is practically independent of the degree of branching.

(3) The assumption that saturated oils could be considered as mixtures of *n*-alkanes, *iso*-alkanes, and mono- and poly-cyclic six carbon ring naphthenes with one alkyl group.

For the investigation of mixtures of saturated hydrocarbons it was desirable to abandon the molecular refraction and the molecular parachor. Instead of these functions the specific functions, namely $\frac{n^2 - 1}{n^2 + 2}\frac{1}{d}$ and $\frac{\sigma^{\frac{1}{4}}}{d}$, were respectively used.

* MS received 27 February 1956.

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In their method Leendertse and Waterman determined in the first place the " true " number of rings of the saturated oil fraction (R^r_T) with the specific refraction–molecular weight method.[6] Use was made of a diagram in which calculated specific refractions of several homologous series of saturated hydrocarbons (*n*-alkanes, monocyclic and polycyclic naphthenes) were plotted against molecular weight. The specific refractions were calculated from the atomic refractions of Eisenlohr (C = 2·418, H = 1·100); later,[7] these values were corrected and the following atomic refractions were used: C = 2·400, H = 1·114. After measuring the value of n, d, and M of the saturated oil fraction, the specific refraction was calculated and plotted in the diagram. The average number of rings per molecule was determined by linear interpolation between the curves. Secondly, starting from the atomic parachor values of Mumford and Phillips (C = 9·0, H = 15·5, the increment for six carbon ring 0·8, and the increment for tertiary carbon atom −3·0) a specific parachor–molecular weight diagram was constructed. In this diagram the specific parachor of *n*-alkanes, monocyclic and several polycyclic six carbon ring naphthenes with one alkyl group were plotted against molecular weight. By determining the specific parachor and the molecular weight of the saturated oil fraction, the " apparent " number of rings (R^p_T) was found by linear interpolation between the curves.

The difference in ring number ($R^p_T - R^r_T$) gave an indication regarding the degree of branching in the oil investigated. It was shown that a difference of 0·1 ring number corresponded to one branching in the molecule.

ADJUSTMENT OF THE ANALYSIS FOR 70° C

In order to study the degree of branching in oils obtained by platforming of paraffin wax, Leendertse's method was applied to these products. However, the following adjustments of the method were necessary:

(1) A specific parachor diagram and a specific refraction diagram were constructed for 70° C instead of 20° C.

(2) The position of the curves in these diagrams was not calculated from average atomic increments, but the curves represent experimental data of *n*-alkanes and *n*-alkyl*cyclo*hexanes at 70° C.

(3) The influence of chain branching on the specific refraction is too high to be neglected. This effect was therefore taken into account.

The adjustments mentioned are discussed below.

(1) As the greater part of the investigated oils were solid at room temperature, measurement of the physical constants had to be carried out at elevated temperatures, *e.g.* 70° C. However, the temperature dependence of the specific refraction and the specific parachor is of such an order that diagrams valid at 70° C differ considerably from diagrams valid at 20° C. Table I shows data on specific refraction and molecular refraction and specific parachor and molecular parachor of some pure hydrocarbons. These values were calculated from tables as given by the API Project 44.[8] The diagrams used in this investigation were constructed by plotting the specific refractions and specific parachors of the *n*-alkanes and *n*-alkyl*cyclo*hexanes at 70° C against $1000/M$. This is shown in Fig 1 (*a* and *b*), where also the lines valid at 20° C are drawn. Fig 1 (*a*) also shows the diagram used by Leendertse (atomic refractions of Eisenlohr) and the diagram based on revised atomic refractions (van Nes and van Westen). Fig 1 (*b*) also shows the diagram calculated by Leendertse from the atomic parachors of Mumford and Phillips. The lines of the *n*-alkanes must intersect the lines of the *n*-alkyl*cyclo*hexanes when M is infinite or when $1000/M = 0$.

These limiting values of the specific refraction and the specific parachor may be calculated in the following way:

As the molecular refraction is an additive function, the specific refraction of an *n*-alkane C_nH_{2n+2} with infinite molecular weight must be equal to:

$$\lim_{n\to\infty} \frac{nR_{CH_2} + 2R_H}{14{\cdot}026n + 2{\cdot}016} = \frac{R_{CH_2}}{14{\cdot}026}$$

in which

R_{CH_2} = the average group contribution of the CH_2 group.

R_H = the average group contribution of an H-atom.

The specific refractions of the *n*-alkyl*cyclo*hexanes must be constant and equal to

$$\frac{nR_{CH_2}}{14{\cdot}026n} = \frac{R_{CH_2}}{14{\cdot}026}$$

From the data on the molecular refraction of n-C_7 – n-C_{20} at 70° C, it appears that R_{CH_2} is equal to 4·655 so that the limiting value of the specific refraction at 70° C is equal to (4·655/14·026) = 0·3319.

At 20° C the value of R_{CH_2} appears to be 4·642 and the limiting value of the specific refraction 0·3310.

As the specific refraction was determined with an accuracy from one to two units in the fourth decimal, its temperature dependence in the temperature range 20°–70° C cannot be neglected.

From the molecular parachor data of n-C_7 – n-C_{20} it appears that the average CH_2 group contribution at 70° C and at 20° C has a value of respectively 40·4 and 40·0. The limiting values of the specific parachor at 70° and 20° C are therefore equal to (40·4/14·026) = 2·88 and (40·0/14·026) = 2·85, respectively.

From Table I it follows that the CH_2 group contribution of the parachor is not absolutely constant. Other investigators[9] have found that the CH_2 contribution becomes greater with increasing molecular weight. The calculated limiting values may therefore be too low. As the specific parachor was determined with an

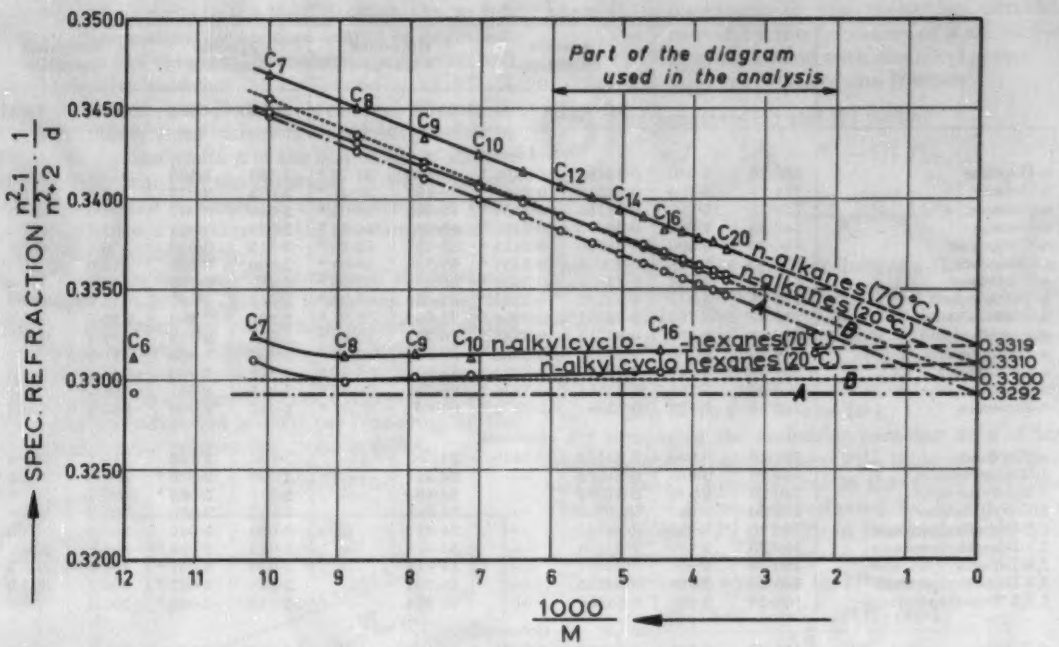


FIG 1 (*a*)

SPECIFIC REFRACTION–MOLECULAR WEIGHT DIAGRAM

A-lines calculated from the atomic refractions of Eisenlohr (C = 2·418, H = 1·100), both at 20° C; B-lines calculated from revised atomic refractions (C = 2·400, H = 1·114), both at 20° C

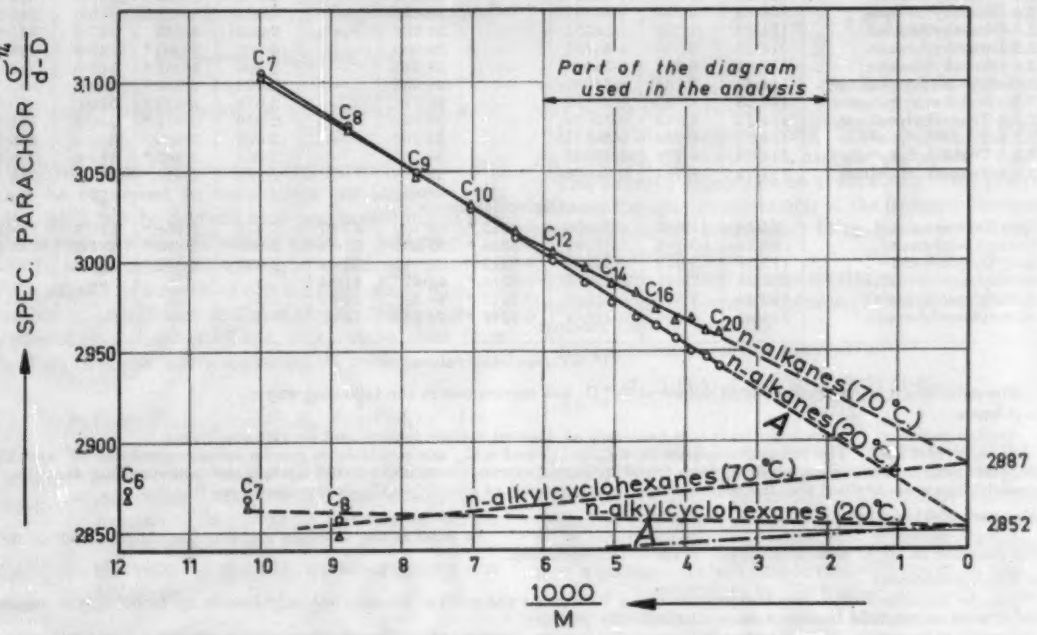


FIG 1 (*b*)

SPECIFIC PARACHOR–MOLECULAR WEIGHT DIAGRAM

A-lines calculated from the atomic parachors of Mumford and Phillips

TABLE I

Compound	M	$\frac{1000}{M}$	Specific refraction		Molecular refraction		Specific parachor		Molecular parachor	
			20° C	70° C	20° C	70° C	20° C	70° C	20° C	70° C
n-Alkanes										
n-Heptane	100·20	9·980	0·34482	0·3469 *	34·550	34·76 *	3·105	3·103	311·1	310·9
n-Octane	114·23	8·754	0·34312	0·3450 *	39·192	39·41 *	3·075	3·073	351·2	351·0
n-Nocane	128·25	7·797	0·34185	0·3434 *	43·842	44·04 *	3·049	3·047	391·0	390·8
n-Decane	142·28	7·028	0·34075	0·3425 *	48·481	48·73 *	3·029	3·031	431·0	431·2
n-Undecane	156·30	6·398	0·33990	0·3415 *	53·127	53·38 *	3·013	3·016	470·9	471·4
n-Dodecane	170·33	5·871	0·33913	0·3407 *	57·764	58·03 *	3·000	3·005	511·0	511·8
n-Tridecane	184·36	5·424	0·33854	0·3401 *	62·412	62·70 *	2·988	2·996	550·9	552·3
n-Tetradecane	198·38	5·041	0·33793	0·3394 *	67·039	67·33 *	2·977	2·987	590·6	592·6
n-Pentadecane	212·41	4·708	0·33751	0·3390 *	71·690	72·01 *	2·969	2·982	630·6	633·4
n-Hexadecane	226·44	4·416	0·33711	0·3383 *	76·333	76·60 *	2·964	2·973	671·1	673·2
n-Heptadecane	240·46	4·159	0·3367	0·3382 *	80·95	81·32 *	2·957	2·966	711·0	713·2
n-Octadecane	254·49	3·929	0·3364	0·3378 *	85·60	85·97 *	2·952	2·968	751·3	755·3
n-Nonadecane	268·51	3·724	0·3361	0·3376 *	90·25	90·65 *	2·947	2·961	791·3	795·1
n-Eicosane	282·54	3·539	0·3358	0·3372 *	94·89	95·27 *	2·942	2·960	831·2	836·3
Heptanes										
n-Heptane	100·20	9·980	0·34482	0·3469	34·550	—	3·105	3·103	311·1	310·9
2-Methylhexane	100·20	9·980	0·34522	—	34·591	—	3·090	3·079 *	309·6	308·5 *
3-Methylhexane	100·20	9·980	0·34392	—	34·460	—	3·071	3·065 *	307·7	307·1 *
3-Ethylpentane	100·20	9·980	0·34215	—	34·283	—	3·047	3·050	305·3	305·6
2,2-Dimethylpentane	100·20	9·980	0·34548	—	34·617	—	3·060	3·049	306·6	305·5
2,3-Dimethylpentane	100·20	9·980	0·34256	—	34·324	—	3·042	3·036 *	304·8	304·2 *
2,4-Dimethylpentane	100·20	9·980	0·34551	—	34·619	—	3·070	3·057 *	307·6	306·3 *
3,3-Dimethylpentane	100·20	9·980	0·34265	—	34·332	—	3·036	3·027 *	304·2	303·3 *
2,2,3-Trimethylbutane	100·20	9·980	0·34306	—	34·374	—	3·018	3·003 *	302·4	300·9 *
Octanes										
n-Octane	114·23	8·754	0·34312	0·3450	39·192	—	3·075	3·073	351·2	351·0
2-Methylheptane	114·23	8·754	0·34346	—	39·231	—	3·053	3·050 *	348·7	348·4 *
3-Methylheptane	114·23	8·754	0·34231	—	39·100	—	3·040	3·038 *	347·2	347·0 *
4-Methylheptane	114·23	8·754	0·34246	—	39·117	—	3·039	3·035 *	347·1	346·7 *
3-Ethylhexane	114·23	8·754	0·34094	—	38·944	—	3·018	3·018 *	344·7	344·7 *
2,2-Dimethylhexane	114·23	8·754	0·34364	—	39·252	—	3·027	3·027 *	345·8	345·8 *
2,3-Dimethylhexane	114·23	8·754	0·34127	—	38·981	—	3·006	3·005 *	343·4	343·3 *
2,4-Dimethylhexane	114·23	8·754	0·34257	—	39·130	—	3·022	3·022 *	345·2	345·2 *
2,5-Dimethylhexane	114·23	8·754	0·34371	—	39·260	—	3·040	3·045	347·3	347·8
3,3-Dimethylhexane	114·23	8·754	0·34151	—	39·009	—	3·002	3·000 *	342·9	342·7 *
3,4-Dimethylhexane	114·23	8·754	0·34008	—	38·845	—	2·999	3·001 *	342·6	342·8 *
2-Methyl-3-ethylpentane	114·23	8·754	0·34000	—	38·836	—	2·995	2·991 *	342·1	341·7 *
3-Methyl-3-ethylpentane	114·23	8·754	0·33896	—	38·717	—	2·978	2·970 *	340·2	339·3 *
2,2,3-Trimethylpentane	114·23	8·754	0·34078	—	38·925	—	2·979	2·971 *	340·3	339·4 *
2,2,4-Trimethylpentane	114·23	8·754	0·34373	—	39·262	—	3·009	3·005	343·7	343·3
2,3,3-Trimethylpentane	114·23	8·754	0·33935	—	38·762	—	2·968	2·962 *	339·0	338·3 *
2,3,4-Trimethylpentane	114·23	8·754	0·34028	—	38·868	—	2·982	2·979 *	340·6	340·3 *
n-*Alkyl*cyclo*hexanes*										
*cyclo*Hexane	84·16	11·882	0·32926	0·3312 *	27·709	27·87 *	2·873	2·868 *	241·8	241·4 *
Methyl*cyclo*hexane	98·18	10·185	0·33105	0·3324 *	32·503	32·64 *	2·868	2·863 *	281·6	281·1 *
Ethyl*cyclo*hexane	112·21	8·912	0·32988	0·3313 *	37·015	37·18 *	2·857	2·847 *	320·6	319·5 *
n-Propyl*cyclo*hexane	126·24	7·921	0·33016	0·3314 *	41·677	41·84 *	—	—	—	—
n-Butyl*cyclo*hexane	140·26	7·130	0·33026	0·3312 *	46·322	46·45 *	—	—	—	—
n-Decyl*cyclo*hexane	224·42	4·456	0·33043	0·3316 *	74·155	74·42 *	—	—	—	—

* Extrapolated values.

The calculation of the extrapolated values at 70° C was carried out in the following way:

n-*Alkanes*

Specific parachor. No extrapolation was necessary as data on surface tension and density are known.

Specific refraction. The refractive indices of n-C_7–n-C_{12} and n-C_{16} are available as precise measurements at 20° and 25° C (five decimals). The values at 70° C were found by linear extrapolation and plotted against the corresponding densities. A straight line was obtained and the values of the refractive indices of n-C_{13}–n-C_{20} determined from this line.

Heptanes and Octanes

Specific parachor. The surface tensions are known at 70° C. As most of the densities are only known up to 50° or 60° C, the densities at 70° C were determined by linear extrapolation.

n-*Alkyl*cyclo*hexanes*

Specific parachor. The densities are known at 70° C. As the surface tensions are only known up to 60° C, the values at 70° C were determined by linear extrapolation.

Specific refraction. The refractive indices at 70° C were determined by linear extrapolation of the values of the precise measurements at 20° and 25° C.

Owing to these extrapolations the position of the n-alkanes and n-alkyl*cyclo*hexanes lines in the diagrams (especially the specific parachor line of the n-alkyl*cyclo*hexanes) is not absolutely certain.

accuracy of six units in the third decimal, also in this case the temperature dependence cannot be neglected.

(2) From the values of the molecular refraction and the molecular parachor of n-C_7 — n-C_{20} at 70° C, average atomic contributions of C and H can be derived. With these values it would be possible to calculate, *e.g.* the position of the line of the n-alkanes in the diagrams. As the constancy of the CH_2 contribution of the parachor is disputable it is more correct to draw a line through the points representing the experimental data.

(3) From the molecular refractions of the heptanes and octanes at 20° C (Table I) it appears that on the whole chain branching causes also a lowering of the molecular refraction. Counting the influence of a quaternary carbon atom as caused by two tertiary carbon atoms, it appears that the average lowering of the molecular refraction is 0·057 per branching for the heptanes, for the octanes this value is 0·089.

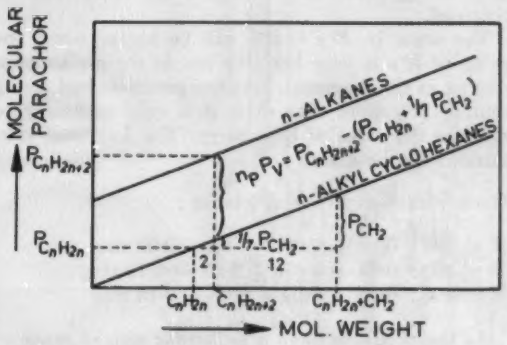


FIG 1 (*c*)

GRAPHICAL REPRESENTATION OF THE FORMULA FOR n_pP_v

The determined difference in ring number ($R^p_T - R'_T$) must be expressed in branchings per molecule. In Fig 1 (*c*) it will be derived that one branching in a n-alkane causes a ring difference equal to 0·09 ring.

If P_v is the average lowering in molecular parachor of a n-alkane as a result of one branching and n_p is the number of branchings in the n-alkane that causes an apparent ring number of one, it becomes clear from Fig 1 (*c*) that the following equation holds :

$$n_pP_v = P_{C_nH_{2n+2}} - (P_{C_nH_{2n}} + \frac{1}{7}P_{CH_2}) \quad (1)$$

$P_{C_nH_{2n+2}}$ = molecular parachor of the n-alkane.
$P_{C_nH_{2n}}$ = molecular parachor of the n-alkyl*cyclo*hexane with the same number of carbon atoms as the n-alkane.
P_{CH_2} = the value of the CH_2 parachor group contribution.

In view of the additivity of the parachor function, one may write

$$P_{C_nH_{2n+2}} - 2P_H + P_r = P_{C_nH_{2n}} \quad (2)$$

where P_r = increment of the molecular parachor caused by the formation of a six carbon ring naphthene with one alkyl group.
P_H = parachor value of one H-atom.

Combining equations (1) and (2) yields :

$$n_pP_v = 2P_H - P_r - 1/7\ P_{CH_2}$$

or

$$n_p = \frac{2P_H - P_r - 1/7\ P_{CH_2}}{P_v} \quad (3)$$

From the molecular parachor data of n-C_7 — n-C_{11} at 70° C it appears that the average value of P_{CH_2} in this range is 40·1. The value of $2P_H$ can be obtained by subtracting n times the value of P_{CH_2} from the value of $P_{C_nH_{2n+2}}$. In doing this it will appear that P_H = 15·0. The atomic parachor value of C is apparently $P_{CH_2} - 2P_H = 40{\cdot}1 - 30{\cdot}0 = 10{\cdot}1$.

By comparing the molecular parachor data of the isomeric heptanes and octanes with those of n-heptane and n-octane it appears that in this range $P_v = 3{\cdot}5$. The value of P_r can be evaluated by subtracting n times P_{CH_2} from $P_{C_nH_{2n}}$. From the data on methyl- and ethyl*cyclo*hexane it appears that $P_r = -0{\cdot}5$.

Substitution in equation (3) gives

$$n_p = \frac{(2)\ (15{\cdot}0) + 0{\cdot}5 - (1/7)\ (40{\cdot}1)}{3{\cdot}5} = 7{\cdot}1$$

or one branching in a n-alkane causes a lowering of $1/7{\cdot}1 = 0{\cdot}14$ ring in the specific parachor diagram.

The same derivation can be applied for the specific refraction at 70° C, so that

$$n_R = \frac{2R_H - R_r - 1/7\ R_{CH_2}}{R_v}$$

where R_H, R_r, R_{CH_2}, and R_v are defined in the same way as for the parachor.

It can be calculated from Table I that at 70° C $R_H = 1{\cdot}085$, $R_r = -0{\cdot}008$, and $R_{CH_2} = 4{\cdot}655$.

The value of R_v cannot be evaluated for 70° C as no data on the specific refraction of the isomeric heptanes and octanes are available. It is, however, plausible that the value of R_v will not vary much with the temperature. From the molecular refractions of nine heptanes and seventeen octanes (Table I) at 20° C, it appears that $R_v = 0{\cdot}073$.

By approximation one may write

$$n_R = \frac{(2)\ (1{\cdot}085) + 0{\cdot}008 - (1/7)\ (4{\cdot}655)}{0{\cdot}073} = 20{\cdot}7$$

or one branching in a n-alkane causes a lowering of $1/20{\cdot}7 = 0{\cdot}05$ ring in the specific refraction diagram. The presence of one branching in a n-alkane will cause therefore a ring difference of $0{\cdot}14 - 0{\cdot}05 = 0{\cdot}09$ ring. Therefore, owing to the presence of eleven branchings in a n-alkane one will find a ring difference of one.

Due to lack of data in the higher molecular weight range, the derivation mentioned above was carried out for the lower molecular weight range. By applying the method to the products it was assumed that the result of the derivation (eleven branchings for

$(R^p_T - R^r_T) = 1$) is also valid for higher molecular weights.

ACCURACY OF THE METHOD

The following physical constants are measured :

n, d, σ, and M. The precision of our measurements is :

for n : $\pm 0{\cdot}0002$
for d : $\pm 0{\cdot}0002$ (g/ml)
for σ : $\pm 0{\cdot}2$ (dynes/cm)
for M : ± 2 per cent

With these data the following calculation of errors can be carried out :

relative error in $\frac{n^2-1}{n^2+2}$: 0·04 per cent for $n = 1{\cdot}42$

" " d : 0·03 per cent for $d = 0{\cdot}77$ g/ml

" " $r = \frac{n^2-1}{n^2+2}\frac{1}{d}$: 0·07 per cent, *i.e.* $\pm 0{\cdot}0002$ for $r = 0{\cdot}34$

At a value in the specific refraction diagram of

$M = 200$, this corresponds with 0·03 ring
$M = 300$, " " " 0·04 "
$M = 400$, " " " 0·05 "

For the specific parachor an analogous calculation can be carried out :

relative error in σ : 0·8 per cent for $\sigma = 25{\cdot}0$ dynes/cm

" " $\sigma^{\frac{1}{4}}$: 0·2 per cent for $\sigma = 25{\cdot}0$ "

" " d : 0·03 per cent for $d = 0{\cdot}77$ g/ml

" " $p = \frac{\sigma^{\frac{1}{4}}}{d}$: 0·23 per cent, or approx 0·2 per cent.

When $p = 2{\cdot}9$ the absolute error will be 0·006. At a value in the specific parachor diagram of

$M = 200$, this corresponds with 0·05 ring
$M = 300$, " " " 0·075 "
$M = 400$, " " " 0·10 "

Up to the present time, the influence of an error in M was not discussed. An error in M caused an incorrect reading of the ring content in both the specific refraction diagram and the specific parachor diagram. In the calculation of the average number of branchings, however, the value of the difference in ring content $(R^p_T - R^r_T)$ was used. For this reason the relative error in M plays no important role in the determination of the number of branchings per molecule.

This is explained by the following example. A substance with a molecular weight of 200, a value of $R^r_T = 0{\cdot}15$ and $R^p_T = 0{\cdot}45$ is considered. $(R^p_T - R^r_T)$ is then 0·30. If the relative error in M is 2 per cent, M can have a value of 204 or 196. From the diagrams it can be read, that for

$M = 196$ $R^r_T = 0{\cdot}164$ $R^p_T = 0{\cdot}459$ $R^p_T - R^r_T = 0{\cdot}295$
$M = 204$ $R^r_T = 0{\cdot}133$ $R^p_T = 0{\cdot}443$ $R^p_T - R^r_T = 0{\cdot}310$

For this reason, the error in $R^p_T - R^r_T$, as a result of the inaccuracy of M, will be maximal 0·01 ring. For $M = 300 \pm 6$ and $M = 400 \pm 8$ the same result is obtained.

The error in $R^p_T - R^r_T$ will be higher when the value of R^r_T is very low (the line of the n-alkanes is sloping in the diagram). As the products had a ring content R^r_T more than 0·15, it is only necessary to consider the value of 0·01 ring. The following conclusions can be drawn :

The accuracy of $R^p_T - R^r_T$ is for :

$M = 200$: 0·03 + 0·05 + 0·01 = 0·09 ring
$M = 300$: 0·04 + 0·075 + 0·01 = 0·12 ring
$M = 400$: 0·05 + 0·10 + 0·01 = 0·16 ring

As the products have a molecular weight range of 300–400, the average accuracy of $R^p_T - R^r_T$ is 0·14 ring. The average accuracy in the number of branchings per molecule is therefore $0{\cdot}14 \times 11 = 1{\cdot}5$. It can be noted, however, that in the authors' case the accuracy must be higher, as the ring content figures are read from average curves. These average curves were obtained from a series of distillation fractions of one product. As an approximation it can be said that the accuracy of the method considered in this investigation is one branching per molecule.

PART II. PLATFORMING OF PARAFFIN WAX

INTRODUCTION

Several investigators [10, 11] have studied the platforming of paraffin wax and found that a part of the reaction product could be purified to a low pour point oil, suitable for low temperature lubricants. As no structural details of the oils obtained were mentioned, the authors wanted to investigate the composition of the reaction product and the influence of the temperature, contact time, and molar ratio H_2/wax thereon.

EXPERIMENTAL

Catalyst

Aluminium *iso*propylate was hydrolysed in boiling water and diluted hydrochloric acid added to the suspension. A colloidal solution of platinum disulphide was prepared by passing hydrogen sulphide through a solution of chloroplatinic acid in water. The resulting colloidal solution was thoroughly mixed with the aluminium hydroxide suspension and the

combined solution oxidized with hydrogen peroxide. After evaporating the water, the mass was dried at 90° C during 14 hr, heated at 160° C during 14 hr, and calcined at 600° C during 12 hr. The resulting catalyst consisted of coarse pieces (3–4 mm) and contained 0·1 per cent platinum and 1·5 per cent chlorine.

was charged to the preheater by a high-pressure displacement pump. At the entry of the preheater the cycle gas, consisting mainly of hydrogen, joined the paraffin feed. After passing the preheater the combined feed entered the top of the reactor, a steel tube with a length of 75 cm and internal diameter of 3·8 cm.

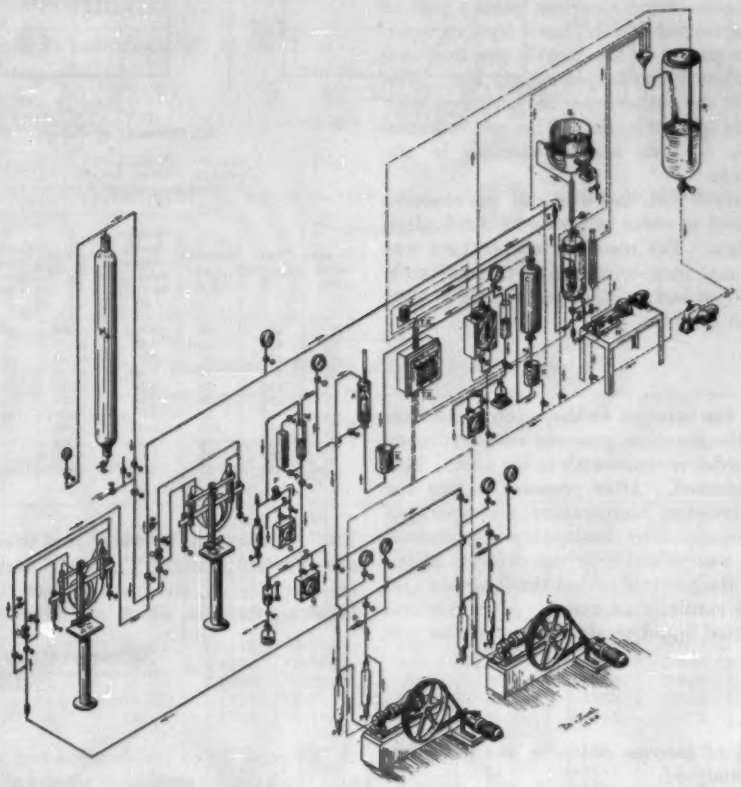


FIG 2

PILOT PLANT DIAGRAM

A—level controller; B—melting vessel; C—reactor; D—safety valve; E—non-return valve; F—back pressure; G—gas-meter; H—feed-pump; J—preheater; K—cooler; L—recycle pumps; M—separators; O—orifice plate; P—circulation pump; R—warm-water boiler; T.K.—thermocouples

Paraffin Wax

The feedstock consisted of commercial white paraffin wax with a molecular weight range of 310–530. The mean molecular weight of the wax was 375, the melting range 52°–54° C, the boiling range 160°–250° C at 1 mm Hg and the density at 70° C 0·7719.

Apparatus

A flow diagram of the semi-technical high-pressure unit is shown in Fig 2. The paraffin wax was molten in a steam jacketed vessel and filtered to remove impurities. The filtered wax was stored in a calibrated feed tank, which was kept at 70° C. The liquid wax

The reactor was heated externally by means of electric heating wires. In the middle of the reactor a catalyst bed of 25 cm was placed and the remaining free space in the top and the bottom of the reactor was filled with porcelain rings. The reaction product was cooled to 70° C by a water condenser and separated from the cycle gas in a high-pressure separator. The liquid products were collected in a bottle and the evolving dissolved gas was passed through a wet gas-meter. If there is a considerable cracking the cycle gas is purified in the following way. After cooling to 20° C the condensed light hydrocarbons are separated from the cycle gas in a second high-pressure separator equipped

with an automatic level recorder. From the second high-pressure separator the liquid products are let down to a middle-pressure separator. The pressure in this system was kept at 10 atm by an automatic pressure controller. The liquid products were collected in a bottle and the evolving dissolved gas passed through a gas-meter.

When the density of the cycle gas became too high owing to the presence of hydrocarbon gases a part of the cycle gas was vented and replaced by hydrogen. Two orifices were placed in the recycle gas line, one before and one after the hydrogen supply line. The pressure-drop over the orifices can be measured with two mercury-filled gas balances. The gas balances are very suitable to note sudden changes in the recirculation system.

All lines in contact with the wax and the reaction product were heated in order to prevent solidification of the paraffin wax. The reaction temperature was measured with an iron–constantan thermocouple placed in the catalyst bed. Other temperatures were also measured and recorded.

Procedure

After charging the catalyst to the reactor, the unit was brought to the reaction pressure with hydrogen and blown off in order to remove air in the unit. This operation was repeated. After pressure testing the unit, the desired pressure, temperature, and hydrogen flow were established. The feed-pump was started and paraffin wax was passed over the catalyst at the desired rate. In the pre-test period the feed rate and temperature were carefully adjusted. After removal of the pre-test period liquid product, the test run was begun.

Method of analysis

As the amount of gaseous products was negligible the gas was not analysed.

The unsaturation of the reaction products was determined by the bromine value according to McIlhiney.[12] It appeared that the reaction products were practically saturated. By distilling the reaction products it appeared that no appreciable amount of light hydrocarbons was present. The reaction products were hydrogenated in an autoclave in order to saturate any present olefinic bonds (200° C, 200 atm, 1 hr, 20 per cent " nickel on kieselguhr " catalyst).

By means of the formolite reaction [13] it was shown that the hydrogenated reaction products did not contain aromatic compounds.

The hydrogenated products and the starting material were distilled in vacuum in an apparatus with ground glass joints. In order to obtain a separation use was made of a Claisen distillation head with a fractionating side arm of 20 cm. The fractions so obtained were analysed for molecular weight, density, surface tension, and refractive index. Densities were determined in pycnometers, molecular weights by measuring freezing-point depressions in *cyclo*hexane, refractive indices with an Abbe refractometer, and surface tensions according to the ring method (apparatus of Cenco-du Nouy).[14]

From these data the degree of branching is determined according to the method discussed in Part I.

CONDITIONS

In Table II the conditions of the experiments are shown.

TABLE II

Platforming of Paraffin Wax

Catalyst: Pt–Al_2O_3–Cl
Catalyst volume: 300 ml.
Duration pre-test period and test run: 4 hour

Experiment no.	Temperature, °C	Pressure Atm (P_t)	Weight hourly space velocity kg/L/hr (a)	Gas rate 1 H_2/kg (b)	Contact-time seconds (t)	Molar ratio H_2/wax	Partial pressure of paraffin wax Atm
T_1	410	52	1·04	5,260	10·1	88	0·58
T_2	420	52	1·01	5,310	10·2	89	0·58
T_3	435	52	0·97	5,440	10·2	91	0·56
T_4	450	52	1·00	5,160	10·2	86	0·60
P_1	432	32	0·99	3,210	10·3	54	0·58
P_2	435	52	1·12	4,720	10·1	79	0·65
P_3	435	72	1·01	7,360	10·1	121	0·59
P_4	435	102	0·96	10,910	10·1	183	0·56
C_1	435	52	1·13	3,330	13·3	59	0·87
C_2	435	52	0·89	3,600	16·4	61	0·83
C_3	435	52	0·75	3,460	20·5	58	0·88

The relationship between the total pressure (P_t), absolute temperature (T), weight hourly space velocity (a), gas rate (b), and contact time (t) is given by the following formula, which can be easily derived

$$t = \frac{(982800)\,(P_t)\,(E)}{(T)\,(a)\left(b + \dfrac{22400}{M}\right)}$$

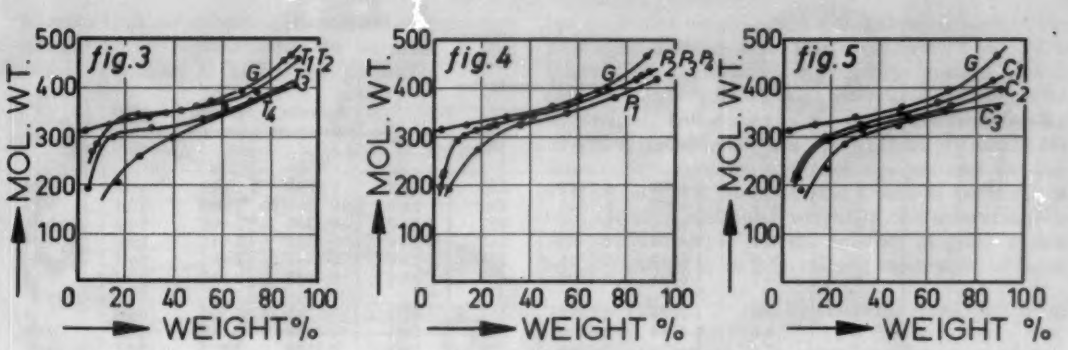
The porosity of the catalyst bed (E) is about 0·75 and the average molecular weight of the paraffin wax (M) is 375. The different runs were done in the order mentioned. The activity of the catalyst after about 90 hr had not decreased very much.

DISCUSSION OF THE RESULTS

Table III shows distillation data of the hydrogenated reaction products and the starting material.

By plotting the weight percentage distilled against the average molecular weight of the fractions the degree of cracking in the reaction products can be revealed. Figs 3, 4, and 5 show the influence of temperature, reaction pressure, and contact time on the hydrocracking reaction. It appears that longer contact times, lower molar ratios H_2/wax, and higher temperatures favour hydrocracking.

The specific refractions and the specific parachors of the distillation fractions are shown in Table III and plotted against $1000/M$ in Figs 6 (a and b), 7 (a and b),



FIGS 3, 4, AND 5

INFLUENCE OF TEMPERATURE, MOLAR RATIO H_2/WAX, AND CONTACT TIME ON HYDROCRACKING

G—paraffin wax

TABLE III

Distillation of Paraffin Wax and Reaction Products

Experiment no.	Distillation		Physical constants				Specific refraction	Specific parachor	1000/M	R_F n–d–M analysis
	Fraction no.	Weight, %	n_D^{70}	d_4^{70}	M	σ^{70}				
Paraffin wax	1	5·6	1·4269	0·7642	315	25·3	0·3359	2·935	3·17	0·01
	2	15·7	1·4273	0·7645	325	25·4	0·3360	2·936	3·08	−0·04
	3	17·7	1·4288	0·7675	340	25·8	0·3358	2·937	2·94	−0·04
	4	20·6	1·4306	0·7718	362	26·1	0·3351	2·929	2·76	0·00
	5	16·9	1·4328	0·7750	396	26·5	0·3352	2·928	2·53	0·08
	6	23·3	1·4364	0·7826	467	27·0	0·3343	2·913	2·14	0·06
T_1	1	15·4	1·4241	0·7599	287	24·8	0·3359	2·937	3·48	0·09
	2	19·0	1·4283	0·7666	347	25·5	0·3358	2·931	2·88	−0·09
	3	16·8	1·4299	0·7698	355	25·6	0·3355	2·922	2·82	−0·04
	4	19·3	1·4319	0·7734	365	26·3	0·3353	2·928	2·74	0·01
	5	29·5	1·4354	0·7807	459	26·8	0·3345	2·914	2·18	−0·10
T_2	1	12·7	1·4221	0·7562	271	24·0	0·3361	2·927	3·69	0·10
	2	15·4	1·4280	0·7663	341	25·4	0·3357	2·930	2·93	−0·06
	3	16·7	1·4294	0·7688	349	25·6	0·3356	2·926	2·87	−0·03
	4	19·7	1·4310	0·7722	376	25·9	0·3352	2·921	2·66	−0·05
	5	18·0	1·4329	0·7758	392	26·2	0·3349	2·916	2·55	−0·01
	6	17·5	1·4363	0·7828	460	26·5	0·3342	2·898	2·17	−0·02
T_3	1	8·8	1·4119	0·7376	193	21·8	0·3373	2·929	5·18	0·26
	2	12·6	1·4258	0·7641	302	24·5	0·3352	2·912	3·31	0·14
	3	16·9	1·4286	0·7685	314	24·9	0·3352	2·907	3·19	0·16
	4	24·7	1·4295	0·7702	336	25·2	0·3351	2·909	2·98	0·10
	5	17·3	1·4319	0·7757	373	25·6	0·3343	2·900	2·68	0·13
	6	19·7	1·4356	0·7819	406	25·9	0·3341	2·885	2·46	0·16
T_4	1	1·7	—	—	—	—	—	—	—	—
	2	10·9	1·4043	0·7254	184	20·2	0·3374	2·923	5·44	0·20
	3	8·9	1·4142	0·7433	207	22·0	0·3363	2·914	4·83	0·29
	4	9·4	1·4224	0·7579	261	23·2	0·3356	2·896	3·83	0·22
	5	15·6	1·4276	0·7675	298	23·9	0·3349	2·881	3·36	0·24
	6	23·8	1·4302	0·7726	344	24·5	0·3345	2·880	2·91	0·17
	7	29·6	1·4331	0·7784	398	25·0	0·3339	2·873	2·51	0·14
P_1	1	12·5	1·4117	0·7374	194	21·2	0·3372	2·910	5·16	0·26
	2	13·6	1·4260	0·7638	274	24·0	0·3355	2·898	3·65	0·24
	3	19·2	1·4290	0·7688	326	24·3	0·3353	2·888	3·07	0·09
	4	19·9	1·4304	0·7718	352	25·1	0·3350	2·900	2·84	0·07
	5	19·7	1·4325	0·7760	381	25·3	0·3346	2·890	2·63	0·08
	6	15·0	1·4361	0·7827	420	25·7	0·3341	2·877	2·38	0·13

TABLE III—*continued*

Experiment no.	Distillation		Physical constants				Specific refraction	Specific parachor	$\frac{1000}{M}$	R_T n–d–M analysis
	Fraction no.	Weight %	n_D^{70}	d_4^{70}	M	σ^{70}				
P_2	1	8·2	1·4158	0·7447	220	22·2	0·3368	2·915	4·55	0·20
	2	10·1	1·4263	0·7648	306	24·3	0·3352	2·903	3·27	0·13
	3	14·7	1·4286	0·7678	327	24·9	0·3355	2·909	3·06	0·05
	4	16·7	1·4297	0·7699	345	25·4	0·3353	2·916	2·90	0·03
	5	21·6	1·4313	0·7735	375	25·5	0·3348	2·905	2·67	0·02
	6	28·7	1·4351	0·7806	425	25·8	0·3343	2·887	2·35	0·03
P_3	1	5·6	1·4104	0·7334	197	21·4	0·3381	2·933	5·08	0·15
	2	8·5	1·4244	0·7606	296	24·1	0·3358	2·913	3·38	0·06
	3	17·3	1·4278	0·7664	322	24·8	0·3356	2·912	3·11	0·05
	4	20·6	1·4294	0·7697	348	25·4	0·3352	2·917	2·87	0·03
	5	16·2	1·4312	0·7734	377	25·6	0·3348	2·908	2·65	0·02
	6	31·7	1·4347	0·7800	418	26·0	0·3343	2·895	2·39	0·05
P_4	1	9·0	1·4161	0·7450	228	22·8	0·3369	2·933	4·39	0·14
	2	17·9	1·4272	0·7655	317	24·7	0·3355	2·912	3·16	0·06
	3	20·2	1·4292	0·7689	340	25·6	0·3354	2·925	2·94	0·03
	4	16·9	1·4313	0·7732	368	25·8	0·3350	2·915	2·72	0·03
	5	13·9	1·4324	0·7754	401	25·6	0·3348	2·901	2·49	−0·04
	6	22·1	1·4349	0·7804	432	25·8	0·3343	2·888	2·32	0·01
C_1	1	12·2	1·4152	0·7415	226	22·2	0·3379	2·927	4·43	0·05
	2	11·3	1·4271	0·7646	298	24·7	0·3359	2·916	3·36	0·11
	3	18·0	1·4290	0·7679	326	25·1	0·3357	2·915	3·07	0·04
	4	14·0	1·4308	0·7719	348	25·4	0·3352	2·908	2·87	0·06
	5	17·0	1·4316	0·7739	371	25·6	0·3349	2·907	2·70	0·04
	6	27·5	1·4349	0·7798	416	25·9	0·3346	2·893	2·40	0·03
C_2	1	12·8	1·4124	0·7375	218	21·5	0·3377	2·920	4·59	0·07
	2	11·7	1·4260	0·7639	294	24·3	0·3354	2·906	3·40	0·15
	3	17·9	1·4284	0·7689	321	25·0	0·3349	2·908	3·12	0·16
	4	17·7	1·4301	0·7712	340	25·0	0·3350	2·899	2·94	0·11
	5	19·0	1·4318	0·7745	366	25·4	0·3348	2·899	2·73	0·09
	6	20·8	1·4351	0·7806	399	25·7	0·3343	2·884	2·51	0·13
C_3	1	2·3	—	—	—	—	—	—	—	—
	2	11·5	1·4069	0·7275	189	20·1	0·3383	2·911	5·29	0·13
	3	10·3	1·4206	0·7546	238	22·9	0·3358	2·899	4·20	0·28
	4	15·5	1·4273	0·7671	312	24·3	0·3349	2·894	3·21	0·17
	5	17·6	1·4291	0·7708	325	24·6	0·3345	2·889	3·08	0·21
	6	19·7	1·4303	0·7732	353	25·1	0·3343	2·895	2·83	0·16
	7	23·3	1·4344	0·7801	362	25·6	0·3341	2·883	2·76	0·28

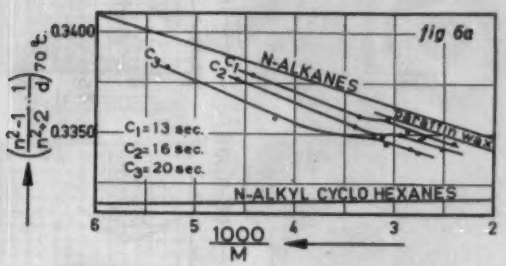
and 8 (*a* and *b*). The discontinuity in the curves at a molecular weight of about 300 (initial molecular weight of the starting material = 310) is a result of the presence of unconverted wax in these fractions.

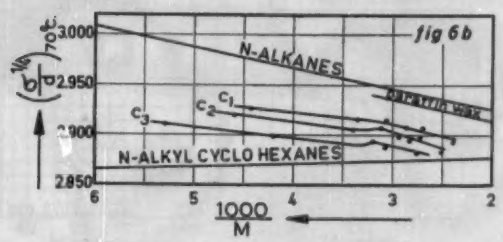
By linear interpolation between the lines of the *n*-alkanes and the *n*-alkyl*cyclo*hexanes at several values of M, R^r_T and R^p_T were determined for each experiment and the average number of branchings calculated by multiplying $(R^p_T - R^r_T)$ by eleven. This is shown in Figs 9 (*b*, *c*, and *d*), 10 (*b*, *c*, and *d*), and 11 (*b*, *c*, and *d*). It appears from Figs 9 (*d*), 10 (*d*), and 11 (*d*) that the application of higher temperatures and lower molar ratios H_2/wax (lower hydrogen partial pressure) favour the isomerization reaction. However, in these cases also the hydrocracking reaction becomes more pronounced. The application of longer contact times have little influence on the isomerization, while hydrocracking is increased.

In Part I it is stated that the specific refraction is sensible for both rings and branchings. Therefore no complete information about the cyclization reaction can be obtained from Figs 9 (*b*), 10 (*b*), and 11 (*b*), where R^r_T is shown for the experiments. However, the average number of rings per molecule in an oil fraction can be calculated from the values of n, d, and M.[7] These values are shown in Table III and plotted against M in Figs 9 (*a*), 10 (*a*), and 11 (*a*). By comparing the curves of R^r_T and R_T in the specific refraction diagram, it appears that on the whole R^r_T is greater than R_T, which is another indication that chain branching causes a small apparent degree of cyclization.

In regard to the cyclization reaction it appears from Figs 9 (*a*), 10 (*a*), and 11 (*a*) that this reaction occurs to a limited extent only. An increase of temperature and contact time causes a higher degree of cyclization in the reaction products, while the application of higher pressures suppresses the cyclization reaction.

In order to select an optimal isomerization condition a quantitative comparison has to be made of the degree of branching in the reaction products.

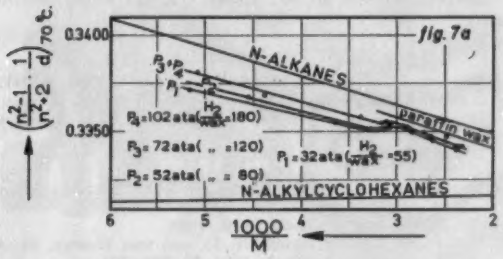


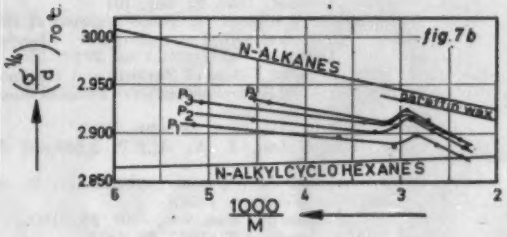


FIGS 6 (*a*) and (*b*)

INFLUENCE OF CONTACT TIME

Specific refraction and specific parachor of the fractions





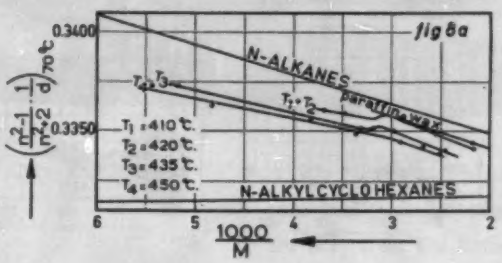
FIGS 7 (*a*) and (*b*)

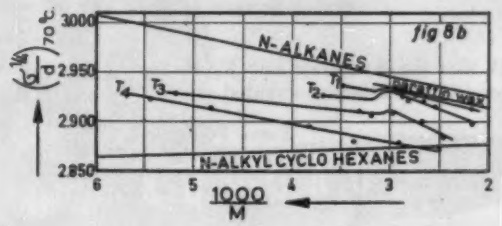
INFLUENCE OF MOLAR RATIO H_2/WAX

Specific refraction and specific parachor of the fractions

Assuming that the reaction products consist entirely of paraffins, the following calculation can be made for each experiment.

In Figs 3, 4, and 5, 100 g of product is considered and the molecular weight range 300–400 (main part of the products) divided into small intervals. For each interval the corresponding quantity (grams) is read and the number of mols of an interval (N) is calculated by dividing this quantity by the average molecular weight of the interval. In Figs 9 (*d*), 10 (*d*), and 11 (*d*) the average number of branchings per mol (or the number of gram atoms tertiary carbon per mol) is read for each molecular weight of the intervals (V). The product $(N)(V)$ is the number of gram atoms tertiary carbon in an interval and summation of these interval values $\sum_{M=300}^{M=400}(N)(V)$ yields the number of gram atoms tertiary carbon in the molecular weight range 300–400. A better picture is obtained if 1410 g of





FIGS 8 (*a*) and (*b*)

INFLUENCE OF REACTION TEMPERATURE

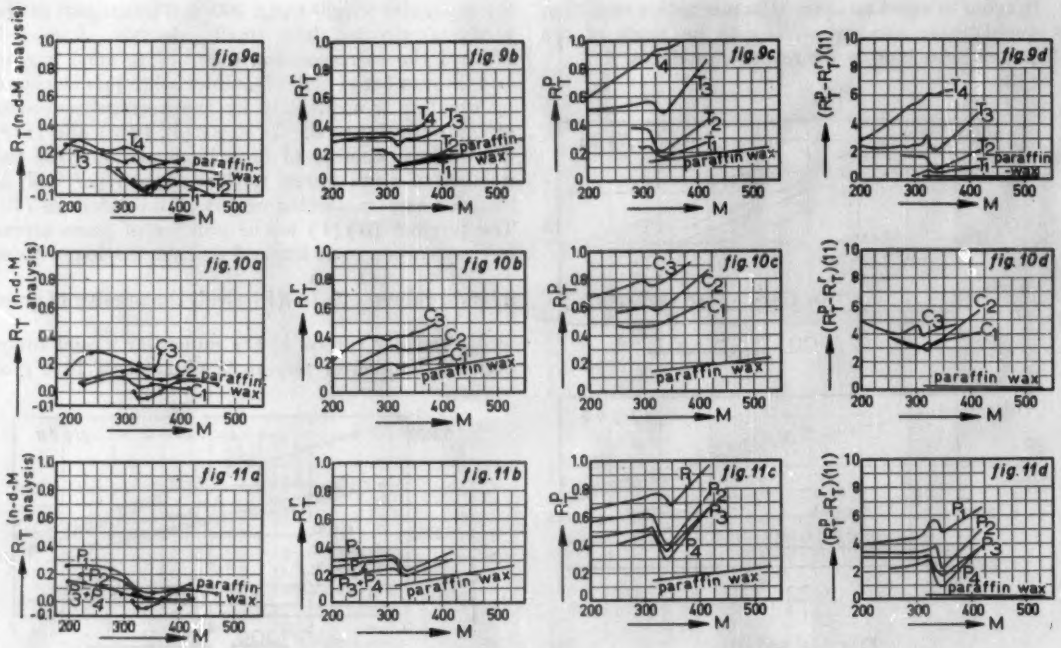
Specific refraction and specific parachor of the fractions

product is considered instead of 100 g, for it can be calculated from the distillation curve of the paraffin wax, that 1410 g of paraffin wax contain 100 gram atoms of carbon. The values of $\sum_{M=300}^{M=400}(N)(V)$ (14·1) are therefore the numbers of gram atoms of tertiary carbon in the range $M = 300$–400, obtained by platforming a quantity of paraffin wax which contains 100 gram atoms of carbon.

Table IV shows the results of this calculation and the absolute errors. It was assumed that the error in V is one branching per mol (see Part I). The error in N is about 2 per cent and can be neglected.

Table IV also shows the amount of cracked material, which is defined as the weight percentage of the product with a molecular weight below 300.

If a maximal isomerization and a cracking loss below 20 per cent is demanded, it appears from Table



FIGS 9, 10, AND 11

AVERAGE NUMBER OF RINGS AND BRANCHINGS PER MOLECULE IN THE REACTION PRODUCTS

IV that the experiments no. T_3, P_2, and C_1 are optimal conditions in the investigated series.

TABLE IV

Experiment no.	Cracked material, %	$\sum_{M=300}^{M=400} (N)(V)(14{\cdot}1)$
Paraffin wax	—	1 ± 3
T_1	9	2 ± 3
T_2	9	4 ± 3
T_3	16	9 ± 3
T_4	39	—
P_1	27	14 ± 3
P_2	11	9 ± 3
P_3	11	7 ± 3
P_4	11	6 ± 3
C_1	18	10 ± 3
C_2	21	11 ± 3
C_3	29	—

ACKNOWLEDGMENTS

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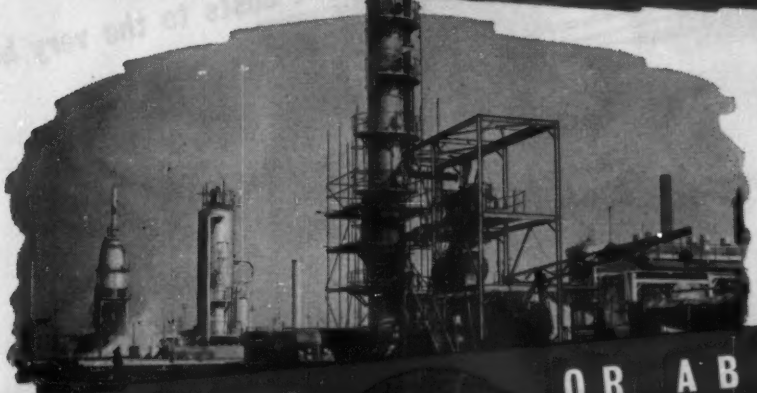

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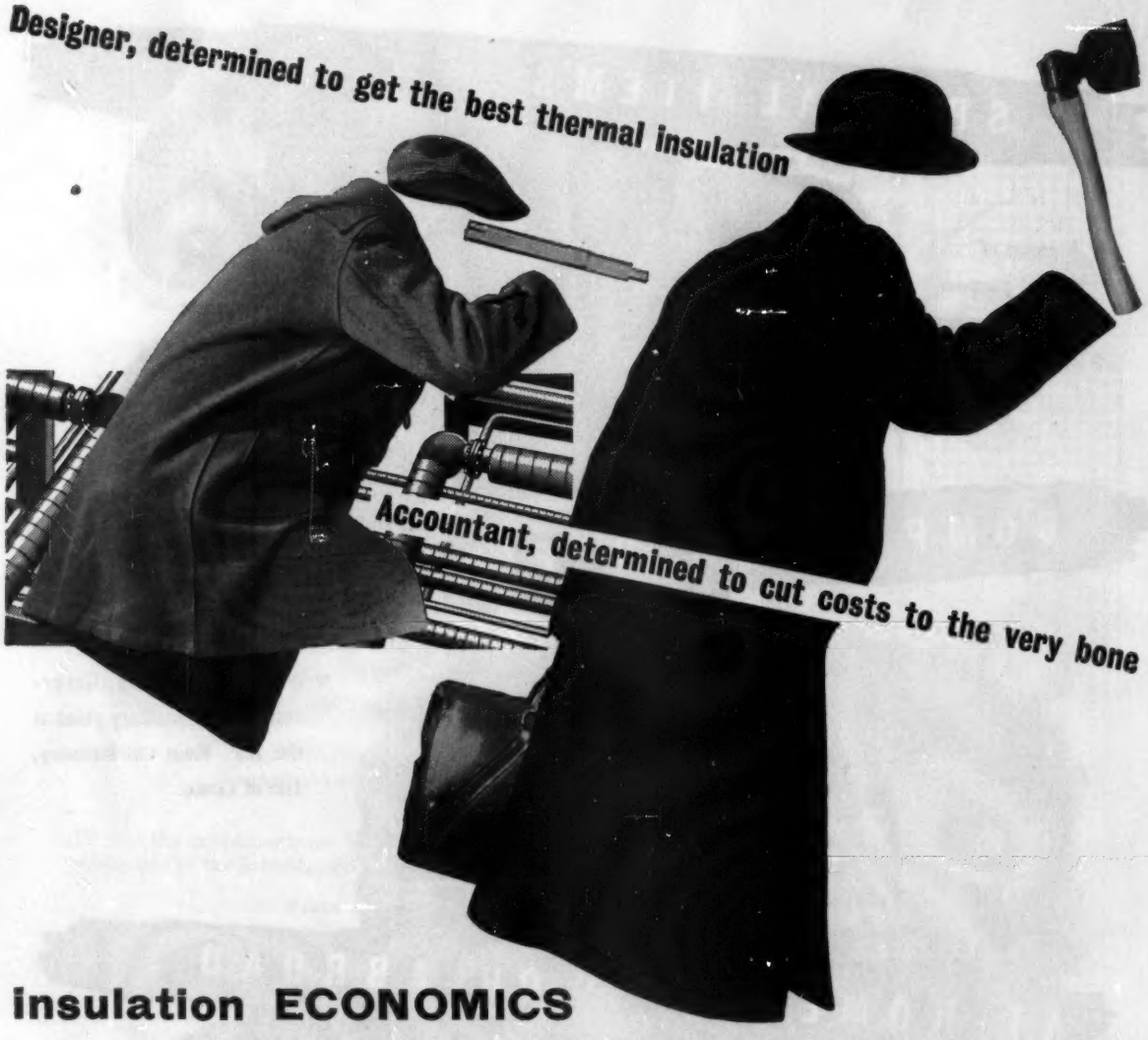

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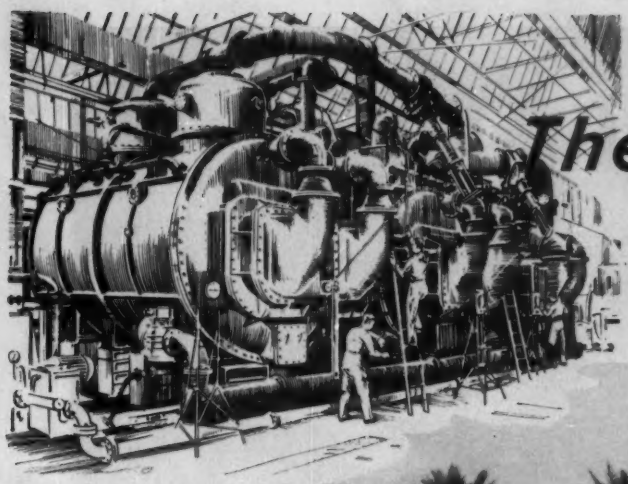

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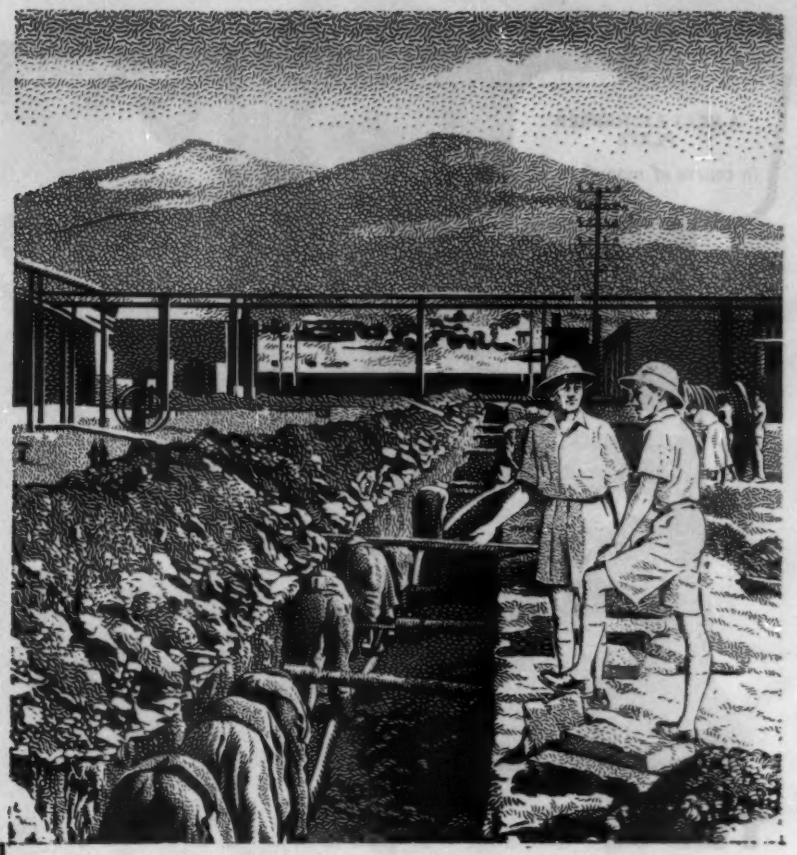

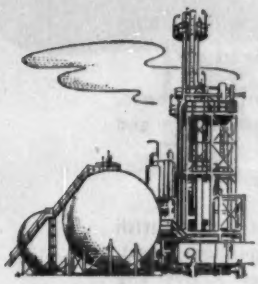

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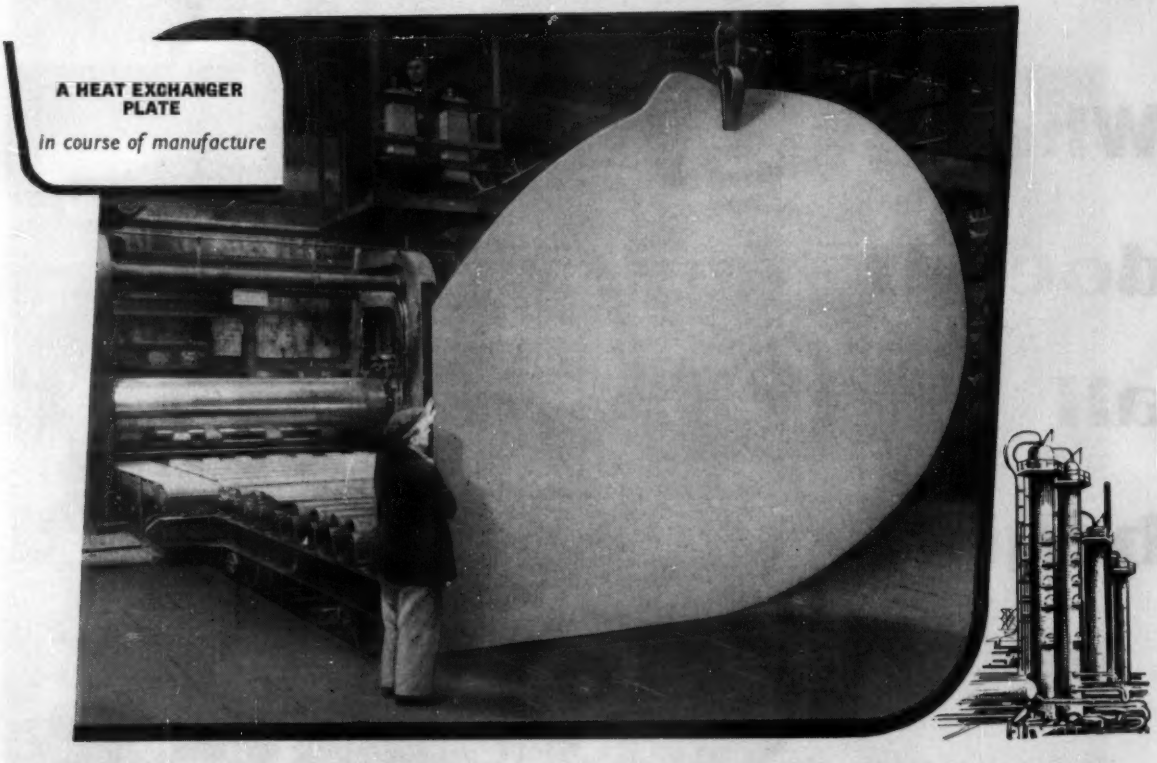

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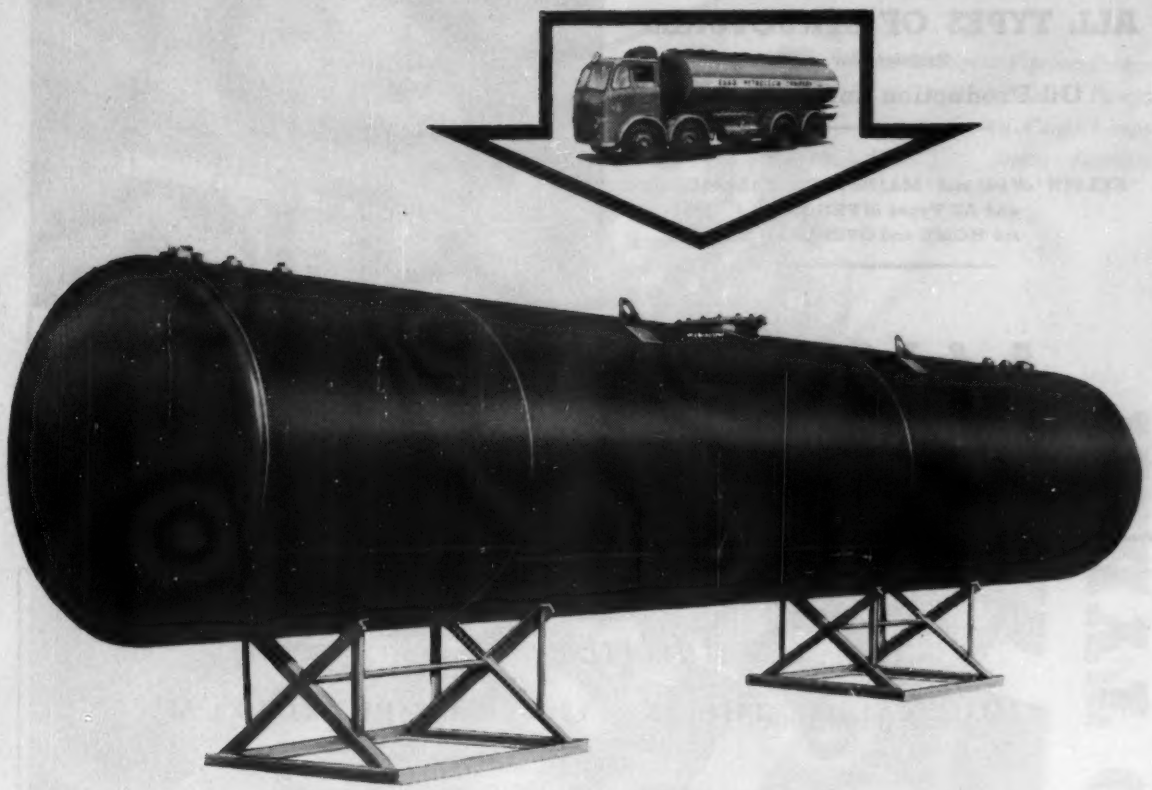

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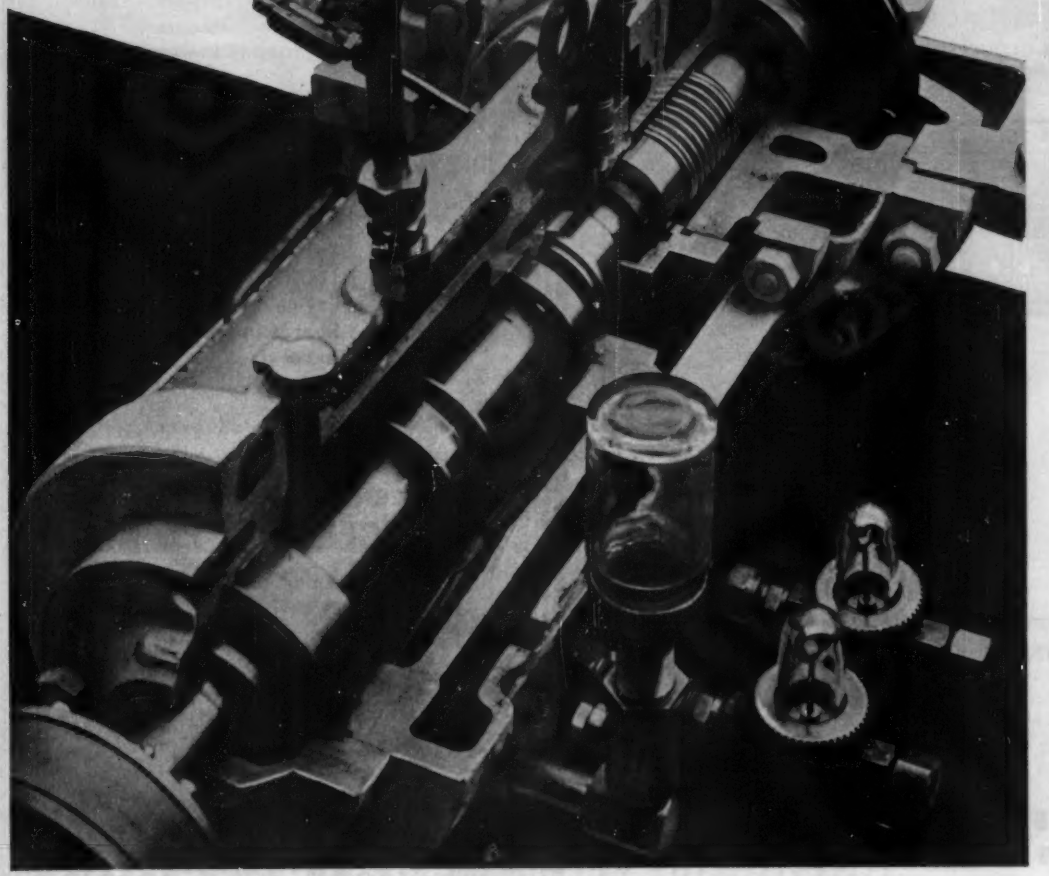

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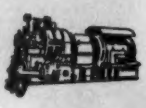

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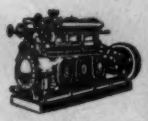

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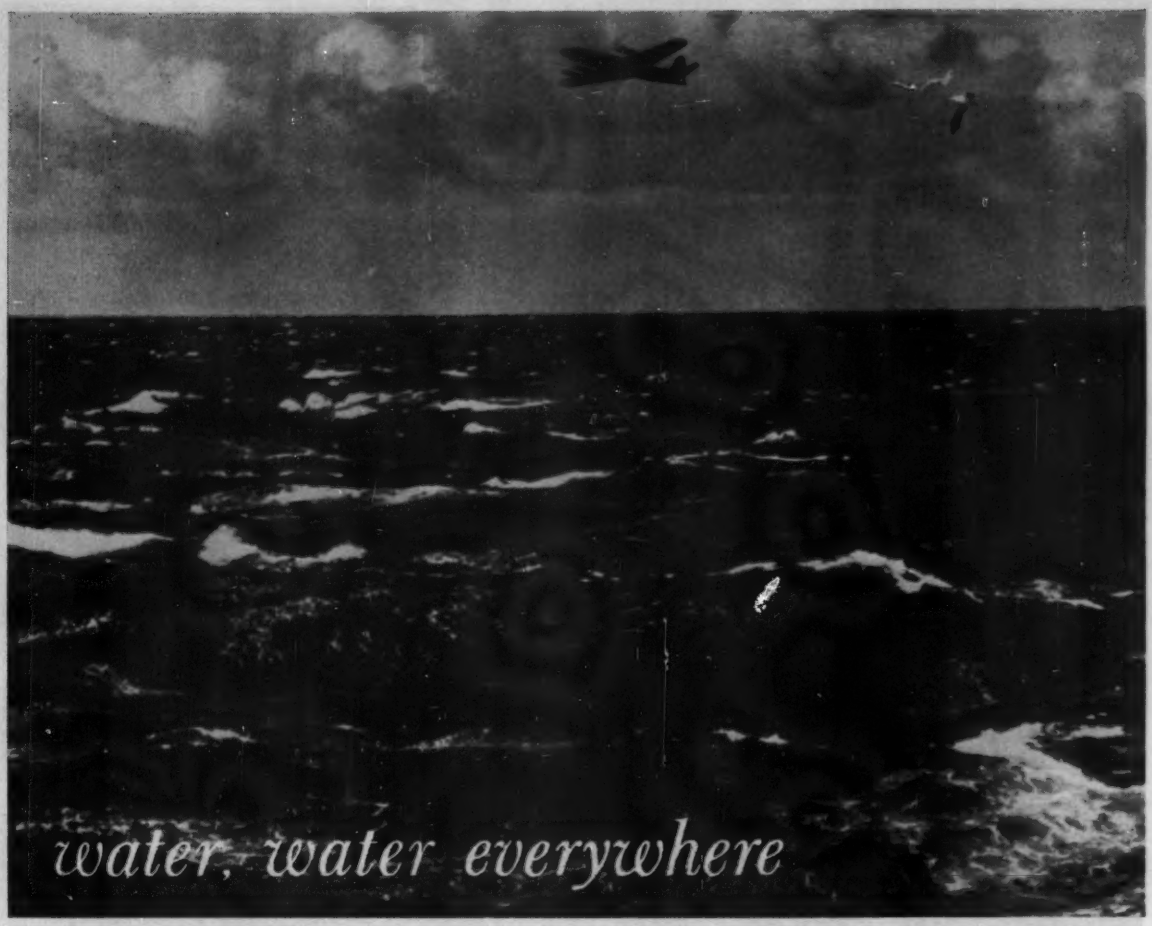

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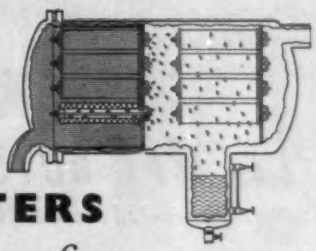

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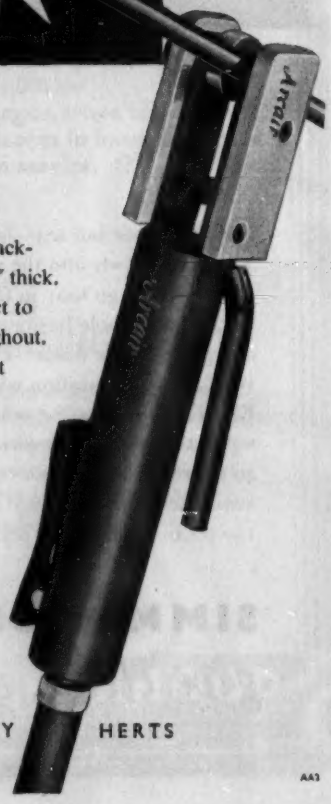

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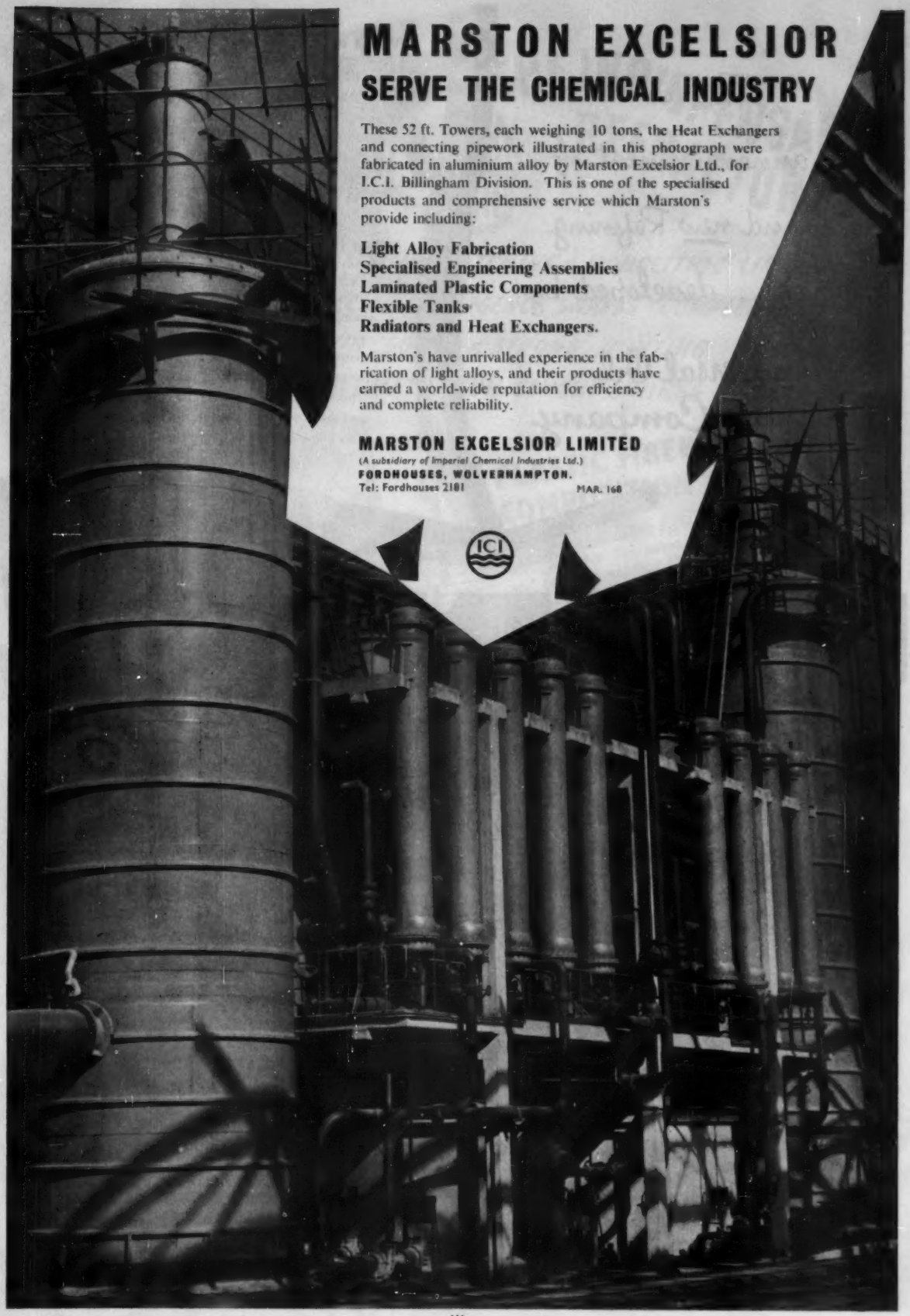

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This is an announcement of a brand new Refining Process... developed by

Universal Oil Products Company

What it is:

PENEX is an entirely new refining process which enables the refiner and natural gasoline manufacturer, for the first time, economically to upgrade his pentane and hexane fractions. It is a simple, continuous process that does not require regeneration, and utilizes a fixed-bed platinum-containing catalyst.

What it does:

PENEX converts the low octane straight chain pentanes and hexanes into the much higher octane iso-compounds, accomplishing this through a clean reaction with little or no loss to by-products. Unconverted portions of the feed stock are separated and recycled to provide the ultimate in octane improvement. This new process employs mild operating conditions, and the non-corrosive nature of the catalyst assures easy and long-sustained operation.

PENEX

TRADEMARK

PENEX offers these advantages:

1. Provides a high octane product with high volatility.
2. Upgrades natural gasoline and light refinery products.
3. Affords mild, continuous operation—maximum simplicity.
4. Clean reaction—insignificant loss to by-products.
5. Economy, both in original investment and day-to-day operation.

PENEX is available NOW!

PENEX is an important advancement in petroleum refining technology. It is ready to be put to work now. All refiners, everywhere, should investigate this new process fully either for early application or for consideration as part of their future planning.

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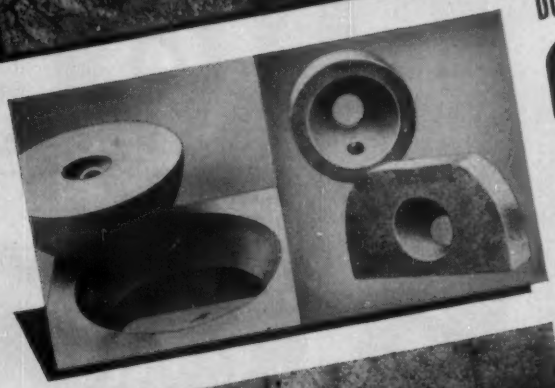
DURAX No 1

PLASTIC FIREBRICK COMPOSITION

Supplied ready mixed for immediate use. Suitable for rammed linings and patching existing Durax No. 1 or firebrick linings. Service temperature range 1300/1650°C.



DURAX No 2

REFRACTORY CONCRETE

For casting in situ and making special shapes. Supplied dry. Special characteristics include—rapid setting as hard as firebrick: pours into position: no permanent volume change: little tendency to spall. Maximum service temperature 1300°C.

DURAX No 3

REFRACTORY CEMENT

A finely ground air setting cement for jointing all types of firebricks. Supplied dry. Special characteristics include—produces thin and strong joints: negligible shrinkage: highly refractory: economical in use. Maximum service temperature 1650°C.

DURAX No 5

GUNNING OR PLASTERING CEMENT

A cement designed for application with a pneumatic gun. Alternatively it may be plastered into position. Durax No. 5 has little rebound loss when applied by gun to Catalytic Regenerators and forms a dense tough lining with a maximum service temperature of 1300°C.

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